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SOIL SCIENCE

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1921
Dr M.W. BEIJERINCK
HOOGLEERAAR
IN MIKROBIOLOGIE
AAN TECHNISCHE HOOGESCHOOL

Martinus Willem Beijerinck
1851–1931

In a country home, close to Gorssel, in the eastern part of Holland, died, on January 1 of this year, Prof. M. W. Beijerinck, whose work in the field of microbiology in general and of soil microbiology in particular is of the greatest theoretical and practical importance.

Beijerinck's first outstanding scientific contribution was of a botanical nature, on a subject bordering between botany and microbiology, namely, his work on the plant galls, which appeared in 1877. His interest in microbiology was aroused in 1885 when he was invited, at the recommendation of Hugo de Vries, by the Netherland Yeast and Alcohol Factory to undertake a series of studies of the growth of microörganisms. This resulted in an investigation, published in 1887, on the rôle of free oxygen in the life processes of the organisms bringing about fermentation. In this work he was a direct successor of Pasteur, who 25 years previously had elucidated the principles of anaerobiosis as "life without oxygen."

It was, however, in 1888, that Beijerinck announced to the world the isolation of a bacterium concerned in the formation of nodules on the roots of leguminous plants, the now famous *Bacillus radicicola*. This was the first of a series of brilliant contributions to the subject of soil microbiology, which has helped in attracting universal attention to the rôle of microörganisms in soil processes and plant growth.

In 1895, Beijerinck was appointed professor of bacteriology at the Polytechnical School in Delft. It was in this laboratory that the most outstanding work in microbiology by Beijerinck and his pupils and associates, who came to him in increasing numbers, was carried out. The investigation of the sulfate-reducing bacteria (*Spirillum desulfuricans*) appeared in 1896, of *Azotobacter* in 1901, of the sulfur-oxidizing bacteria (*Thiobacillus* group) in 1903, of the bacteria bringing about denitrification in 1903, all of which are of the greatest importance in soil science. In addition to these, Beijerinck's investigations dealt with the butyl alcohol and butyric acid bacteria, the lactic acid and acetic acid bacteria, the microbes active in the retting of flax, the microorganisms of kefir, as well as with the nutrition of algae, amoebae, yeasts, and fungi, embracing nearly every branch of microbiology. Plant pathology benefited considerably not only from his work on the root galls, but also from his study of the contagious nature of "gummosis" (1882), as well as of the mosaic in tobacco plants ("contagium vivum fluidum").

Beijerinck will always be considered in the history of microbiology as a

pioneer who opened up numerous fields of investigation. In this respect, he is a direct descendant of his likewise great countryman Antonie van Leeuwenhoek. His work was progressing so rapidly, and numerous ideas and discoveries were made in such rapid succession that, although he made several attempts to write an all-embracing book, such as the tentative *Ecology of Microbes*, he never wrote it.

Beijerinck's investigations pointed the way to numerous applications of the activities of microörganisms in natural processes. At an age when the microbes as pathogenic organisms were attracting universal attention, the work of Beijerinck emphasized the useful functions of the numerous microbes in agriculture and in industry. Beijerinck's contributions to soil science bridged the gap between the growth of plants and soil processes, as indicated by his work on the root galls and nodule bacteria. Toward the end of his life he returned to botany, as indicated by his papers on regeneration of buds and position of leaves. Although botany and plant anatomy, microbial physiology and microbial ecology will always be indebted to him for his great contributions to the respective sciences, it is soil microbiology that has benefited most from the work of this man of genius.

His numerous pupils, his still larger number of friends and visitors who have gained from his magnetic personality, and all those who were guided in their work by his ideas and discoveries will deplore deeply the loss that science suffers from the passing of this indefatigable investigator.

SELMAN A. WAKSMAN.

SOIL ORGANIC MATTER-TEMPERATURE RELATIONSHIP IN THE EASTERN UNITED STATES

HANS JENNY

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Received for publication June 7, 1930

In the Great Plains region and in the prairie-timber transition zone the average total nitrogen content of the soil decreases with increasing annual temperature in regions of similar precipitation-evaporation ratios (1, 3).

Since the total nitrogen and the total organic carbon content of the soil form a more or less constant ratio, as demonstrated by Sievers and Holtz, Waksman, and others (5), the organic matter content of the soil should manifest a similar decrease from north to south in relation to temperature.

This paper is a report of a study to determine whether a soil organic matter-temperature relationship can be observed quantitatively. The region selected for this investigation belongs to the eastern United States, including New York, New England, New Jersey, Delaware, Maryland, Virginia, North Carolina, South Carolina, Georgia, Alabama, and Florida. The parent material from which the soils are derived consists partly of igneous and metamorphic rocks, (Piedmont Plateau) and partly of sedimentary deposits (Coastal Plains). The native vegetation has been classified by Shantz as "southern hardwood forest" (oak-pine phase) and "southeastern pine forest" (longleaf-loblolly-slash pines).

Organic matter analyses (total carbon x 1.742) of 18 counties, lying mainly within the Piedmont Plateau and the Atlantic Coastal Plain, were taken from the *Field Operations of the Bureau of Soils 1902 and 1903.* Only predominating, well-drained upland soils of loam and sandy loam textures were considered. Each point in figure 1 represents the average organic matter content of the surface soils of an entire county, which was calculated according to the example given in table 1.

In order to follow the trend of the organic matter-temperature relation north of the Piedmont Plateau and Atlantic Coastal Plain, three counties from New York and New England were included in this investigation. The humidity factors of these counties are somewhat higher, namely N. S. Q.[1] 400–500, than those of the southern counties, which lie between N. S. Q. 300–400. Consequently in fitting the curve, less weight was given to the three northern points in the graph, which would make the slope of the curve even steeper than that shown in figure 1 (see also table 2).

[1] Rainfall divided by absolute saturation deficit of air (2).

The correlation ratio, which is considered to be an index of the dispersion of the points around the curve, has a value of -0.87 ± 0.036. According to the scale of Chaddock, this value indicates a high degree of association between temperature and soil organic matter.

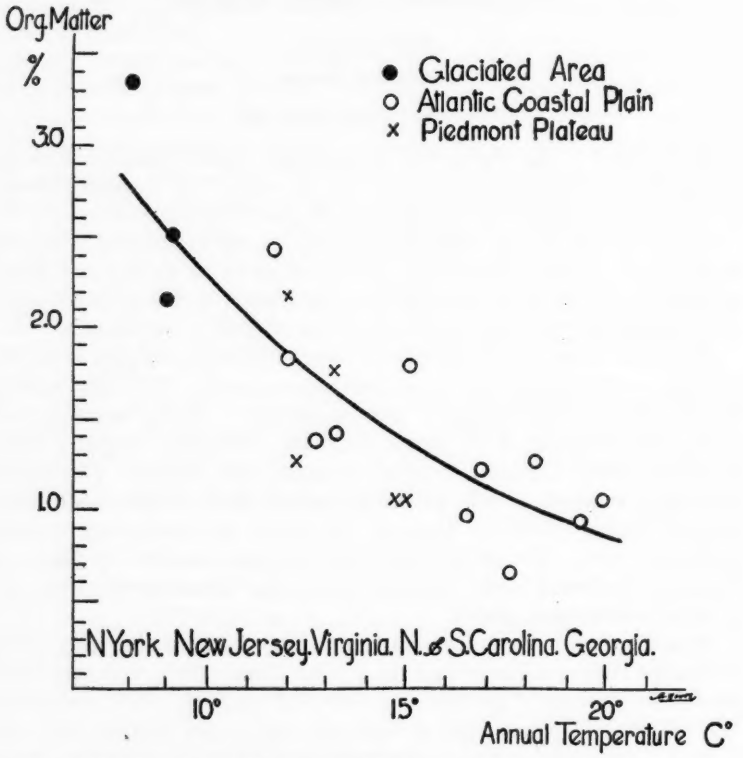

FIG. 1. ORGANIC MATTER-TEMPERATURE-DIAGRAM OF SOILS FROM THE EASTERN UNITED STATES

Each point represents a "county average"

The computation of the "calculated values" in table 2 is based on the empirical formula:

$$O.M. = 6.50\, e^{-0.104\, T_{\bar{a}}^{20}}$$

where $O.\ M.$ means average organic matter content of the surface soils of a county in per cent and T the mean annual temperature of a county in degrees C.

The rule previously observed, that for a fall of 10°C. in annual temperature, the average nitrogen content of the soil increases two to three times, is also valid for the organic matter content of the soils investigated. At 20°C. the

average calculated organic matter content is 0.81 per cent, whereas at 10°C. it reaches 2.30 per cent, which is 2.84 times greater than the lower value at 20°C.

A very interesting property of the soil organic matter-climate relationship becomes evident by comparison of the organic matter figures in table 2 with

TABLE 1

Illustration of the method of calculating the average organic matter content of the soils of a county

Perry County, Alabama. Ann. Temperature 64.5°F. Ann. Humidity factor N. S. Q. about 310.

SOIL TYPES (COSTAL PLAIN SOILS)	PER CENT OF COUNTY AREA	ANALYSES OF ORGANIC MATTER CONTENT		AREA × AVERAGE	AVERAGE ORGANIC MATTER CONTENT OF COUNTY
		Single values	Average		
	per cent	*per cent*	*per cent*		*per cent*
Orangeburg sandy loam.....	40.2	0.38, 0.70, 0.54, 0.67	0.57	$40.2 \times 0.57 = 22.91$	$\frac{27.41}{43.2} =$ 0.63% O.M.
Sassafras sandy loam.....	3.0	2.01, 1.00	1.50	$3.0 \times 1.50 = \underline{4.50}$	
	43.2			27.41	

This method of calculation might be called a mathematical "short cut" of the following reasoning: In calculating the average organic matter content of the county, not only the organic matter content of the various soil types, but also their area, has to be taken into consideration. Thus, in the above example the county organic matter content, if based solely on the analyses or the two soil types, is $\frac{0.57 + 1.50}{2} = 1.035$ per cent, which is not a fair value, because the abnormally high organic matter value of the unimportant soil type Sassafras sandy loam receives too large a share in forming the county average. This error is corrected by using the area of the soil types as "weight." In the above case, the area of Perry County is 487,744 acres. The Orangeburg sandy loam occupies 40.2 per cent, or 196,073 acres, the Sassafras sandy loam 3.0 per cent, or 14,632 acreas. The organic matter percentage multiplied by 20,000 gives the organic matter content in pounds to the acre, $6\frac{2}{3}$ inches deep (2 million pounds of soil), which is 11,400 pounds for the Orangeburg sandy loam and 30,000 pounds for the Sassafras sandy loam. Multiplying pounds of organic matter to the acre by the number of acres gives the total amount of organic matter present in the entire area of the respective soil types. Hence, for Orangeburg sandy loam: $11{,}400 \times 196{,}073 = 2.235 \times 10^9$ pounds, and for the Sassafras sandy loam: $30{,}000 \times 14{,}632 = 0.439 \times 10^9$ pounds. The 210,705 acres (both soil types together) contain therefore 2.674×10^9 pounds of organic matter, or one acre contains 2.674×10^9 divided by 210,705 = 12,691 pounds to the acre. Dividing this value by 20,000 converts the pound to the acre value into the percentage figure, which gives 0.63 per cent organic matter.

the nitrogen values of the timber soils from the Middle West, which were published previously (1, p. 176). The timber soils of Wisconsin, Illinois, Western Kentucky and Tennessee, and Mississippi are subject to annual climatic conditions similar to those of the Atlantic Coast States, consequently,

one might also expect a certain conformity within the soil organic matter constituents of the two regions. Several calculated nitrogen averages of midwestern timber soils are shown in column 3 of table 3; the climatically corresponding organic matter figures from the eastern soils are listed in column 4. Division of the latter values by the conventional humus factor 1.742 gives the percentages of total organic carbon (column 5). If one divides now the carbon figures of the eastern soils by the climatically corresponding nitrogen figures of the midwestern soils, one obtains a surprisingly constant

TABLE 2

Summary of organic matter values

ANNUAL TEMPERATURE		STATE	COUNTY AREA	NUMBER OF SOIL TYPES PER COUNTY	NUMBER OF ANALYSES PER COUNTY	AVERAGE ORGANIC MATTER CONTENT OF LOAMY SOILS PER COUNTY				
						Glaciated region	Piedmont region	Costal plain	Calculated value	Deviation
°F.	°C.					*per cent*	*per cent*	*per cent*	*per cent*	
46.7	8.17	New York	Syracuse	3	8	3.35	....	....	2.78	+0.57
48.2	9.00	Connecticut Valley		4	7	2.16	....	....	2.55	−0.39
48.4	9.11	New York	Big Flats	2	6	2.51	....	....	2.52	−0.01
52.1	10.67	New York	Long Island	3	7	....	....	2.43	2.03	+0.40
53.6	12.00	New Jersey	Trenton	5	14	....	2.18	1.82	1.87	+0.31
										−0.05
53.8	12.17	Virginia	Leesburg	6	13	....	1.27	....	1.83	−0.56
55.0	12.78	Delaware	Dover	2	5	....	....	1.37	1.72	−0.35
55.8	13.22	Virginia	Albemarle	2	5	....	1.74	....	1.64	+0.10
56.0	13.30	Maryland	Worcester	2	6	....	....	1.42	1.63	−0.21
58.7	14.83	N. Carolina	Hickory	2	6	....	1.09	....	1.39	−0.30
59.1	15.06	S. Carolina	Campobello	1	2	....	1.09	....	1.36	−0.27
59.4	15.22	Virginia	Norfolk	3	9	....	....	1.79	1.33	+0.46
61.9	16.61	N. Carolina	Graven	2	6	....	....	0.98	1.16	−0.18
62.5	16.94	S. Carolina	Darlington	5	9	....	....	1.22	1.12	+0.10
63.9	17.72	Alabama	Perry	2	6	....	....	0.63	1.03	−0.40
64.9	18.28	Georgia	Fort Valley	2	4	....	....	1.27	0.97	+0.30
67.0	19.44	Alabama	Mobile	3	7	....	....	0.95	0.86	+0.09
68.0	20.00	Florida	Gadsden	3	8	....	....	1.06	0.81	+0.25

value of about 10.8 (column 6) which represents the well-known carbon-nitrogen ratio. In other words, the eastern organic matter-temperature curve and the midwestern nitrogen temperature curve are identical in that they differ only by a constant, the C/N ratio times 1.742. Multiplying, for example, the calculated average nitrogen content of central Illinois timber soils, which is 0.122 per cent N (at 10°C.), by 10.8 x 1.742 results in an organic matter content of 2.29 per cent. The corresponding organic matter value of the eastern soils at 10°C. is 2.30 per cent. This close agreement is undoubtedly due to the fact that all of the calculated figures are based on averages of large

regions. Taking observed data of smaller areas instead of calculated regional averages, naturally makes the agreement less close. For the particular district of Illinois in question, the analytical averages read as follows: N = 0.124 per cent; C:N ratio = 11.21, organic matter = 2.42 per cent. The difference between calculated and observed organic matter and C:N figures amounts to 5.5 per cent. In this kind of work, dealing with so many uncontrolled variables, an agreement within 10 per cent must be considered satisfactory.

In consideration of the great variation in parent material and age of the soils of the two regions on the one hand, and the uniformity of the soil organic matter conditions on the other, one is led to believe that the nitrogen equilibrium of cultivated soil responds sensitively to the operating climatic factors. Within large regions, having a wide range in climatic conditions, temperature,

TABLE 3

Comparison of the organic matter temperature curve of the eastern United States with the nitrogen temperature curve of the Middle West

TEMPERATURE		CALCULATED NITROGEN CONTENT OF MID-WESTERN SOILS	CALCULATED ORGANIC MATTER CONTENT OF EASTERN SOILS	CALCULATED CARBON CONTENT OF EASTERN SOILS. *O.M.* ÷ 1.742	CARBON NITROGEN RATIO (C/N)
°C.	°F.	*per cent N*	*per cent O.M.*		
8	46.4	0.148	2.83	1.623	11.0
10	50.0	0.121	2.30	1.321	10.9
12	53.6	0.098	1.87	1.073	10.9
14	57.2	0.080	1.52	0.872	10.9
16	60.8	0.066	1.23	0.706	10.7
18	64.4	0.054	1.00	0.574	10.6
20	68.0	0.044	0.81	0.465	10.6
Average.....					10.8

humidity, and vegetation apparently exert a greater influence on soil organic matter constituents of loam soils than does either parent material or age.

SUMMARY[2]

The organic matter content of surface soils of 18 counties in the eastern United States was correlated with annual temperature. It was found that with *increasing* temperature, the organic matter content of the soil *decreases* exponentially.

[2] *Note during print:* In a recent paper on "Some carbon-nitrogen relations in soils" (*Soil Sci.* 30: 257-266, 1930) W. R. Leighty and E. C. Shorey published a series of nitrogen and carbon analyses of cultivated soils from the eastern United States. The data for timbered upland soils of loam and sandy loam texture show a pronounced decrease of nitrogen and organic matter from north to south as seen from the following table:

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(1) JENNY, H. 1929 Relation of temperature to the amount of nitrogen in soils. *Soil Sci.* 27: 169–188.

(2) JENNY, H. 1930 The nitrogen content of the soil as related to the precipitation-evaporation ratio. *Soil Sci.* 29: 193–206.

(3) JENNY, H. 1930 An equation of state for soil nitrogen. *Jour. Phys. Chem.* 34: 1053–1057.

(4) U. S. DEPARTMENT OF AGRICULTURE. Field operations of the Bureau of Soils 1902 and 1903.

(5) WAKSMAN, S. A. 1929 Chemical nature of soil organic matter, methods of analyses, and the rôle of micro-organisms in its formation and decomposition. *Trans. Second Comn. Internatl. Soc. Soil Sci.* (Budapest). A: 172–197.

FOOTNOTE 2—*continued*

Nitrogen-organic matter-temperature relationship in Eastern United States, after data from Leighty and Shorey

STATE	NUMBER OF ANALYSES	APPROXIMATE ANNUAL TEMPERATURE	N	ORGANIC MATTER (C × 1.724)
		°C.	*per cent*	*per cent*
Maine	1	4.0	0.227	5.17
Pennsylvania	4	11.0	0.176	3.12
New York	4	11.2	0.116	2.78
New Jersey	4	11.5	0.125	2.31
Virginia	7	15.0	0.074	1.36
North Carolina	6	16.0	0.047	1.42
South Carolina	4	17.0	0.028	0.92
Georgia	4	18.5	0.044	1.15
Florida	1	20.0	0.041	1.74

SOIL FORMING PROCESSES IN THE HAWAIIAN ISLANDS FROM THE CHEMICAL AND MINERALOGICAL POINTS OF VIEW

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The chemical composition of a soil depends on the nature of the original rock from which the soil is derived, on the nature of the weathering processes, and on the length of the weathering. Some idea of the nature of the processes may be had by comparing the chemical analyses of the original fresh rock and the derived weathered soil.

It is known, in a general way, that the chief effects of weathering in Hawaii are the conversion of aluminum and iron to hydrous oxides and the removal in solution of much of the other constituents.

It is also possible to compare the minerals of the original fresh rock with the minerals of the derived weathered soil. Both sorts of comparisons are undertaken in the present paper.

BASIC DATA

In order to study such processes one would wish for pairs of analyses of the fresh rocks and of the soils derived from them. Such data are lacking. Over a hundred superior analyses of Hawaiian basalts have been made, but the corresponding soil analyses are lacking. Although several hundred soil analyses are available, they were unfortunately made by the inferior process of digestion with hydrochloric acid, which leaves much undetermined matter in the "insoluble residue." One might compare the average of a large number of soil analyses, if superior ones were available, with the average of the rock analyses, but this would be open to the objection that one could not be sure that they represented the same material in the rock and in the soil condition. Moreover, such averages would integrate the effects of a variety of climatic types.

The best data available for such a study are the four pairs of analyses made by Kelley[1] on the fresh cores and on the weathered shells of four spheroidal boulders from gulches in the Wahiawa region of Oahu. Since all refer to one rather small locality they also show the effects of a single type of climate.

[1] KELLEY, W. P. 1912. The function and distribution of manganese in soils and plants, Hawaii Agr. Exp. Sta., Bul. 26. A typographical error in one of the analyses is corrected in bulletin 42 of the same series, Composition of Hawaiian Soil Particles, by W. T. McGeorge, 1917.

These analyses report the amounts of 13 radicals, and appear to have been made by the superior method of complete fusion with sodium carbonate. These pairs of analyses have the advantage that in each pair there has been no admixture of mineral or organic matter from foreign sources, consequently the weathered shells show precisely what happens to materials having the composition of the core. They have the disadvantage that the soil-forming process has not been carried to completion, but they do show the direction in which weathering is working. Another disadvantage, namely, that they represent only one locality and only one type of Hawaiian climate, is counterbalanced by the definiteness for that one locality and climatic type.

TABLE 1

Analyses of rock cores and weathered shells

RADICAL	A	B	C	D	E	F	G	H	I	J
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
SiO_2	52.45	20.29	52.15	24.01	51.98	26.82	52.24	32.00	52.21	25.78
Al_2O_3	11.49	37.97	12.57	36.27	15.85	30.13	16.00	35.28	13.98	34.91
Fe_2O_3	3.66	15.01	3.36	14.29	2.90	16.86	3.73	11.80	3.41	14.49
FeO	6.90	3.22	7.07	3.31	6.84	3.03	5.89	1.53	6.63	2.77
Mn_3O_4	0.36	0.19	0.50	0.43	0.92	0.06	0.68	0.08	0.62	0.19
MgO	5.81	0.20	6.51	0.09	5.61	0.11	5.90	0.14	5.96	0.14
CaO	10.32	0.33	8.54	0.17	9.57	0.22	9.54	0.22	9.49	0.24
K_2O	0.89	0.25	0.84	0.24	0.97	0.46	0.86	0.30	0.89	0.31
Na_2O	2.44	0.27	2.64	0.31	2.70	0.57	2.65	0.61	2.61	0.44
SO_3	0.20	0.78	0.61	0.49	0.51	0.74	0.53	0.70	0.46	0.63
P_2O_5	0.38	0.23	0.28	0.34	0.22	0.19	0.11	0.04	0.25	0.20
TiO_2	4.07	4.69	4.07	4.84	1.50	2.21	1.50	2.13	2.79	3.47
H_2O	1.02	16.84	0.94	15.61	1.04	18.34	0.54	15.06	0.89	16.46
Sum	99.99	100.27	100.08	100.40	100.61	99.74	100.17	99.89	100.19	100.03

A, C, E, and G—Analyses of the four fresh cores of spheroidal boulders.
B, D, F, and H—Analyses of the four corresponding weathered shells.
I—Average of A, C, E, and G.
J—Average of B, D, F, and H.

The nearest station for which climatological data are available is Upper Hoaeae, which has a mean annual rainfall of 34.50 inches. The mean annual temperature is 71.8°F. The warmest month (August) averages 75.6° and the coldest month (January) averages 67.7°F. A standard U. S. Weather Bureau evaporation pan shows an evaporation of about 61 inches a year.

The four pairs of analyses, as reported by McGeorge, are given in table 1, together with averages of the four pairs.

CHEMICAL INTERPRETATION

The fresh, original rock and the weathered derived material can be compared in two ways. Since rocks consist of aggregations of grains of one or more

minerals, the minerals of the rock can be compared with the minerals of the derived material, as one of the methods. The minerals, however, are chemical compounds, and a given element is likely to exist in more than one of the minerals of a rock. Chemical analyses show the amounts of the various radicals in the rock. The second method, then, is to compare the chemical analyses. This will be undertaken first.

In table 2 the averages of table 1 (I and J) are recast so as to total 100 per cent for use in subsequent computations, and also so as to convert Mn_3O_4 to

TABLE 2

Chemical changes during weathering

RADICAL	K	L	M	N	O	P	Q	R
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
SiO_2	52.13	25.77	10.31	−41.82	.....	−80.2	.....	19.8
Al_2O_3	13.96	34.90	13.96	0.00	0.00	.....	.....	100.0
Fe_2O_3	3.40	14.49	5.80	.....	+2.40	.....	+70.3	170.3
FeO	6.62	2.77	1.11	−5.51	.....	−83.2	.....	16.8
MnO	0.58	0.18	0.07	−0.51	.....	−87.9	.....	12.1
MgO	5.95	0.14	0.06	−5.89	.....	−99.0	.....	1.0
CaO	9.47	0.24	0.10	−9.37	.....	−98.9	.....	1.1
K_2O	0.89	0.31	0.12	−0.77	.....	−86.5	.....	13.5
Na_2O	2.61	0.44	0.18	−2.43	.....	−93.1	.....	6.9
SO_3	0.46	0.63	0.25	−0.21	.....	−45.7	.....	54.3
P_2O_5	0.25	0.20	0.08	−0.17	.....	−68.0	.....	32.0
TiO_2	2.79	3.47	1.39	−1.40	.....	−50.2	.....	49.8
H_2O	0.89	16.46	6.58	.....	+5.69	.....	+640.0	728.1
Sum	100.00	100.00	40.01	−68.08	+8.09	.....	.....	.....

K—Recast average of four fresh cores.

L—Recast average of four weathered shells.

M—Preceding recast on the assumption of no change of Al_2O_3. Equals $L \times 0.4000 = L \times \frac{13.96}{34.90}$.

N and O—Losses and gains by weathering in terms of percentage of total fresh cores. Equals M minus K.

P and Q—Losses and gains in terms of percentage of the amount of each radicle originally present. Equals N (or O)/K × 100.

R—Amount of each radicle remaining in terms of percentage of amount of each radicle originally present. Equals M/K × 100.

the equivalent amount of MnO, the more probable form in which manganese enters silicate minerals.

For the present study the averages of the four pairs of analyses are used, since a preliminary study showed that the behavior of each pair was much like the behavior of the other pairs and of the averages.

The arbitrary assumption, in computing column M from columns K and L of table 2, that there has been neither gain nor loss of alumina (Al_2O_3) in weathering, deserves a little discussion. Of the various radicals present, water is

the only one for which we can conceive a source that might supply additions. Atmospheric oxygen also is undoubtedly added and accounts for the apparent increase of ferric oxide (Fe_2O_3)—much of the ferrous oxide (FeO) is oxidized to ferric oxide. There are no conceivable sources for additions the other radicals. Columns K and L show that, excepting water and ferric oxide, alumina has the highest ratio between its amount in the weathered shells and its amount in the fresh cores. This indicates that alumina has suffered the least loss. It is very probable that natural Hawaiian waters contain very little alumina, but the available water analyses give no evidence on this point. They report alumina, if they report it at all, along with ferric oxide, with which it is precipitated and weighed in the usual routine. Since some assumption must underlie the computations, and since the loss of alumina is the smallest, the selected assumption is that there has been no loss or gain of alumina. On this assumption, it appears that 100 parts by weight of the original fresh rock lose about 67 parts by solution (column N) and gain about 6 parts of water by hydration and 1 parts of oxygen by oxidation of ferrous to ferric oxide. Thus, 100 parts of fresh rock give rise to 40 parts of the weathered material. (The total for column N is about 68 whereas the loss by solution just given is 67. The total for column O is about 8, whereas the gains of water and oxygen just given total 7. These discrepancies are due to the shifting of about 1 part of iron from the ferrous to the ferric state.)

Similar studies of other soils have indicated that titania is the most stable constituent. Such is not the case with the analyses here studied. Computation on the assumption of no change of titania would demand greater increases of water and of ferric oxide, and would also demand that the amount of alumina be doubled during the weathering and the amount of sulfur trioxide be increased nearly 11 per cent. It is conceivable that sulfur trioxide might be derived from the gypsum in wind-blown spray, but there is no conceivable source for even a small part of the large increase of alumina demanded. Titania therefore, is less stable than alumina.

It is probable that if oxidizing conditions prevailed throughout the weathering process, iron would be as stable as alumina. Under reducing conditions, however, iron is less stable than alumina. Leith and Mead[2] state on the basis of their studies of the lateritic iron ores of Cuba and the bauxitic aluminum ores of the southern states, that basic rocks under reducing conditions lose iron and give rise to bauxite and gibbsite, hydrous oxides of aluminum. Under moist conditions, with much vegetation to produce reducing conditions, this process removes color producing iron oxides and so gives rather bleached soils in places in Hawaii. Under oxidizing conditions the end product of the weathering of basic rocks is laterite. Leith and Mead ascribe the proverbially rapid weathering of basic rocks to the chemical instability of the lime feldspars, of the pyroxenes, and of the olivines which weather and are dissolved out, causing

[2] LEITH, C. K., AND MEAD, W. J. 1915. Metamorphic Geology, p. 37, Henry Holt & Co.

a porous texture which allows ground water to enter readily and attack other mineral grains.

If the various radicals are considered in the order of decreasing gains, or increasing losses, as compared to the amount of the various radicals in the fresh, original rock, the relative susceptibility of the various radicals is shown.

The following may be said in summarizing the chemical changes:

Water is added in large amounts and is an actual addition.

Oxygen is actually added, and explains the apparent addition of ferric oxide.

The lack of any change in alumina, though due to an arbitrary assumption, indicates that alumina is the most stable radical in the list.

Sulfur trioxide and titania decrease to amounts between three-eights and five-eights of the original amounts.

Phosphorus pentoxide, silica, ferrous oxide, and potash decrease to amounts between one-eighth and three-eighths of the original amounts. Manganous oxide falls just a little outside this group.

Manganous oxide and soda decrease to amounts between one-sixteenth and one-eighth of the original amounts.

Lime and magnesia decrease to about one-hundredth of the amount originally present.

A check might be had on the foregoing conclusions as to the relative amounts of the various radicals removed during the weathering if we could analyze the waters that did the removing. This is obviously impossible, but we can examine the character of other Hawaiian natural waters. The best data available to me for such a check are given by a single analysis of water collected from Kalihi Stream, at an elevation of about 470 feet, on August 16, 1928.

Though these data are the best available at the present moment, it must be remembered that they represent a water from a point removed from the water that weathered the rock by a distance of some 15 miles and by a time that is to be measured in hundreds of years. Moreover the two regions have somewhat different climates and decidedly different topographic characters. As a consequence too close correspondence between them is not to be expected.

The analysis of the Kalihi water is given in part in column Y of table 3. The bicarbonate and nitrate radicals are omitted since they are not included in the rock analyses. The ingredients of this water are in part derived by solution from the rocks and in part from wind-blown sea salt. It is necessary, therefore, to subtract from the total the part derived from the sea, in order to learn what has been derived from the rocks. Column W of table 3 gives the composition of the dissolved matter in sea water. These are adjusted by multiplying by 16/56.292, which brings the value for chlorine to the amount of chlorine in the Kalihi Stream water. Chlorine is used as a basis for this conversion since it is reasonable to assume that none of the chlorine in the Kalihi water is derived from the rocks. By a further adjustment the elemental ingredients reported in the sea water are converted to the equivalent oxides for comparison with the oxides removed from the rock. After this double adjustment the amounts of the salts supplied from sea water to the Kalihi water are those given in column X, table 3.

Column Y of this table gives the analysis of the Kalihi water as reported, and column Z gives this analysis with the elemental ingredients converted to the equivalent oxides. Subtracting the values in column X from those in

TABLE 3

Comparison of materials dissolved in Kalihi stream water with materials lost in weathering as previously calculated

RADICAL	W	X	Y	Z	AA	BB	CC	DD
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
SiO_2	0.000	0.000	26.00	26.00	26.000	59.81	41.82	65.13
Al_2O_3	0.000	0.000	.....	.....	0.000	0.00	0.00	0:00
Fe	0.000	0.000	0.43	.....	.....	.....	.....	.....
Fe_2O_3	.....	.....	.....	0.61	0.61	1.40	3.72	5.79
Mg	3.725	.....	3.8	.....	.....	.....	.....	.....
MgO	.....	1.787	.....	6.30	4.513	10.38	5.89	9.17
Ca	1.197	.....	4.2	.....	.....	.....	.....	.....
CaO	.....	0.865	.....	5.88	5.015	11.54	9.37	14.59
Na	30.593	.....	12.0	.....	.....	.....	.....	.....
Na_2O	.....	11.933	.....	16.17	4.241	9.76	2.43	3.78
K	1.106	.....	0.9	.....	.....	.....	.....	.....
K_2O	.....	0.386	.....	1.08	0.694	1.60	0.77	1.20
SO_4	7.692	.....	5.1	.....	.....	.....	.....	.....
SO_3	.....	1.855	.....	4.25	2.395	5.51	0.21	0.33
Cl	55.222	16.000	16.0	16.00	0.000	0.00	.....	.....
				76.29	43.468	100.00	64.21	100.00

W—Average composition of salts in 77 sea water samples. F. W. Clarke, The Data of Geochemistry, Ed. 4, p. 123, U. S. Geol. Survey, Bull. 695.

X—Same adjusted to oxides instead of elements, and to make chlorine equal to the chlorine in the Kalihi water (column Y).

Y—Composition of Kalihi Stream water (Personal Communication).

Z—Same, adjusted to oxides instead of elements.

AA—Composition of salts in Kalihi water after deducting those derived from salt spray (equals Z-X).

BB—Same as AA, adjusted to total 100.

CC—Material removed in weathering rocks.

DD—Same as CC, adjusted to total 100 for comparison with column BB.

column Z, we get column AA. This is equivalent to subtracting from the Kalihi water the ingredients supplied from sea water so that the remainder, column AA, is the material dissolved from the rocks and soil by the Kalihi water since it fell as rain.

Column CC, repeats columns N and O of table 2, except that the gain of Fe_2O_3 and the loss of FeO are balanced off in terms of like Fe, the net change being expressed as the equivalent Fe_2O_3. Column CC represents the losses as obtained by comparing the fresh and weathered materials.

Column AA totals 43.468 and column CC totals 64.21, and are therefore a little difficult to compare. Comparison would be facilitated if both were adjusted to the same total. In columns BB and DD the data of columns AA and CC, respectively, have been multiplied by suitable factors so that both total 100.

Columns BB and DD, show that there is rather close agreement as to silica, magnesia, lime, and potash; but that there is less good correspondence for ferric oxide, soda, and sulfate. It would appear that the Kalihi water has picked up sodium sulfate in some unexplained way, and has lost some ferric oxide.

MINERALOGICAL INTERPRETATION

The calculation of the mineral composition of a rock from its chemical analysis is often performed by petrologists. The percentages by weight of each radical are divided by the corresponding radical weights. The quotients thus obtained give the relative numbers of the radicals present, which are called the "radical ratios." These are then distributed to form mineral molecules in accordance with certain established standard procedures. The numbers of molecules of each mineral are then multiplied by the molecular weights of the minerals, and the products are the percentages of the minerals in the rock. The standard procedure among petrologists gives comparable results, and the mineral composition thus arbitrarily computed is known as the "norm" of the rock. The norm usually differs from the "mode" or actual mineral composition of the rock.

The averages of the four fresh cores and of the four weathered shells (columns I and J, table 1) are thus treated in tables 4 and 6, with the exception that the standard procedure has been modified in order to make the computed composition more like the known mode of the Hawaiian basalts.

In explanation of the computations, we might consider the treatment of the ferrous oxide and the titania in table 4. The adjusted percentages of these radicals are 6.62 and 2.79, and their radical weights are 71.84 and 80.1, respectively. Dividing the percentages by the radical weights we get $3.40/71.84 = 0.0921$ and $2.79/80.1 = 0.0348$. The quotients are multiplied by 10,000 in order to give integers, which are more convenient to handle. We may say, then, that for every 921 radicals of ferrous oxide there are 348 radicals of titania. There is a mineral in Hawaiian basalts called "ilmenite" whose molecule ($FeO \cdot TiO_2$ or $FeTiO_3$) consists of one radical of ferrous oxide and one radical of titania. So the 348 radicals of titania and 348 of the 921 radicals of ferrous oxide are combined to make 348 molecules of ilmenite. In the lower part of table 4, the 348 molecules of ilmenite again appear, where they are multiplied

by 151.94, the molecular weight of ilmenite, giving a product of 528.7, which by a rounding off and shifting of the decimal point shows that the rock contains 5.29 per cent of the mineral ilmenite.

After 348 radicals of ferrous oxide have been set aside for ilmenite 573

TABLE 4

Computation of norm of average of four fresh cores

RADICAL	PER CENT	RADICAL RATIO	Il.	Ap.	No.	Or.	Ab.	An.	Ma.	METASILICATES				Qz.
										Fe	Ca	Mg	Mn	
SiO_2	52.13	8,680	...	...	228	564	1,500	1,822	...	360	723	1,476	82	1,925
Al_2O_3	13.96	1,369	...	...	114	94	250	911	...	...	...	.....	...	.....
Fe_2O_3	3.40	213	...	...	...	...	.....	.....	213	...	...	.....	...	.....
FeO	6.62	921	348	...	...	...	.....	.....	213	360	...	.....	...	.....
MnO	0.58	82	...	...	...	...	.....	.....	...	...	...	.....	82	.....
MgO	5.95	1,476	...	...	...	...	.....	.....	...	...	...	1,476	...	.....
CaO	9.47	1,688	...	54	...	...	.....	911	...	...	723	.....	...	.....
K_2O	0.89	94	...	...	...	94	.....	.....	...	...	...	.....	...	.....
Na_2O	2.61	421	...	...	171	...	250	.....	...	...	...	.....	...	.....
SO_3	0.46	57	...	...	57	...	.....	.....	...	...	...	.....	...	.....
P_2O_5	0.25	18	...	18	...	...	.....	.....	...	...	...	.....	...	.....
TiO_2	2.79	348	348	...	...	...	.....	.....	...	...	...	.....	...	.....
H_2O	0.89													
	100.00													

MINERAL	COMPOSITION	NUMBER OF MOLECULES	MOLECULAR WEIGHT	PER CENT
Ilmenite	$FeOTiO_2$	348	151.94	5.29
Apatite	$Ca_3P_2O_8 + 1/3CaF_2$	18	336.34	0.61
Noselite	$Na_6Al_4Si_4SO_{16}$	57	710.12	4.05
Orthoclase	$KAlSi_3O_8$*	94	556.49	5.23
Albite	$NaAlSi_3O_8$*	250	524.28	13.11
Anorthite	$CaAl_2Si_2O_8$	911	278.15	25.34
Magnetite	Fe_3O_4	213	231.52	4.93
Iron metasilicate	$FeSiO_3$	360	131.90	4.75
Wollastonite	$CaSiO_3$	723	116.15	8.40
Clinoenstatite	$MgSiO_3$	1,476	100.38	14.82
Rhodonite	$MnSiO_3$	82	130.99	1.07
Quartz	SiO_2	1,925	60.06	11.56
Water	H_2O	.....	.....	0.89
				100.05

* This is half the formula used in the upper part of the table.

remain. Of these, 213 are next set aside to match the 213 radicals of ferric oxide to make magnetite ($FeO \cdot Fe_2O_3$ or Fe_3O_4), leaving 360 to be combined with part of the silica for iron metasilicate ($FeO \cdot SiO_2$ or $FeSiO_3$).

The order in which the radicals are set aside to form various minerals is essentially that which the study of countless rocks has shown to be the order

of crystallization in nature. The relative affinities of the various kinds of radicals for one another are well known for the igneous rocks, but not for the weathered products.

In the fresh cores, all the titania and a proper amount of ferrous oxide are first assigned to ilmenite, which is one of the first minerals to crystallize. Next, enough lime is assigned to the available phosphorus pentoxide to form apatite, also an early forming mineral. The sulphur trioxide surely exists as noselite, or some related mineral. Therefore, suitable amounts of soda, alumina, and silica are assigned to the sulfur trioxide for noselite. At this stage all of the acids, except silica, have been used up. Silica is first assigned, along with proper amounts of alumina, to the strong bases to form the potash and soda feldspars (orthoclase and albite). So far as alumina is still available, the lime feldspar (anorthite) is made, which takes part of the lime and silica. With alumina all gone, the remaining silica is used as far as necessary to make metasilicates of ferrous oxide, lime, magnesia, and manganous oxide. In the preceding discussion one step has been omitted, namely, the assigning of part of the ferrous oxide to the ferric oxide for magnetite. Finally, after all the bases have been assigned, there still remains some silica, which is taken for quartz. In the calculations, the metasilicates are considered independently, but they actually do combine as dual or even trial metasilicates, thus forming a complex group of minerals known as the pyroxenes. Were there not enough silica to go around among the bases, as metasilicates, we would first have satisfied the lime and manganous oxide. Then in accordance with suitable formulas, we would have made partly metasilicates (pyroxenes) and partly orthosilicates (olivines) with the magnesia and ferrous oxide.

The pyroxenes are a series of related metasilicates which usually have lime, magnesia, and ferrous oxide as their basic radicals. The oxides of manganese, the alkalies, zinc, aluminum, and ferric iron form the bases in some rarer varieties. Some are characterized by having a single base: for example, enstatite, which is $MgO \cdot SiO_2$. (This differs from the corresponding orthosilicate, forsterite, $2MgO \cdot SiO_2$, in having twice as much silica in proportion to the magnesia.) Most pyroxenes are either compounds or mixtures of silicates of two or more bases, for example, diopside, which is $MgCaSi_2O_6$. Many pyroxenes are far more complicated. Washington and Merwin[3] give an analysis (table 5) of an augite, a variety of pyroxene, from near the summit of Haleakala.

According to Washington and Merwin the "augite is thus essentially a hedenbergite-diopside with small amounts of acmite, clinoenstatite, and alumina in solid solution."

Undoubtedly all the augites of Hawaii are of much the same complex character as this one.

[3] WASHINGTON, H. S., AND MERWIN, H. E. 1922. Augite of Haleakala, Maui, Hawaiian Islands. *Amer. Jour. Sci.* 3: 117–122.

A rather striking thing in the norm of the fresh cores, given in table 4, is the occurrence of quartz. Quartz does not occur as a primary mineral in the basalts of Hawaii, and yet it is shown in the norm. The probable explanation is that the quartz is present in solid solution in the glass that fills the interstices between the crystalline grains of the other minerals. In the normal sequence of crystallization of various minerals out of a magma, quartz is among the very last to form. It is therefore likely to remain non-crystalline or glassy when cooling, finally brings about the rigid state of glass in the residual melt. Minerals richer in silica than those used in the preceding calculation of the norm are not to be found by microscopic examination of thin sections of Hawaiian rocks.

The steps in calculating the mineral composition of the weathered shells are rather similar, and are set forth in table 6, but the choice of an association

TABLE 5

Chemical analysis and calculated mineral composition of the augite of Haleakala

RADICAL	PER CENT	MINERAL	FORMULA	PER CENT
SiO_2	47.70			
Al_2O_3	6.82			
Fe_2O_3	3.36			
FeO	4.43	Diopside	$CaMgSi_2O_6$	69.12
MnO	0.16	Hedenbergite	$CaFeSi_2O_6$	15.13
MgO	13.34	Acmite	$NaFe^{III}Si_2O_6$	5.08
CaO	21.35	Clinoenstatite	$MgSiO_3$	1.90
K_2O	0.03	Iron metasilicate	$FeSiO_3$	0.40
Na_2O	0.65	Corundum and Hematite	$(Al, Fe)_2O_3$	8.65
TiO_2	1.89			100.28
Cr_2O_3	0.23			
H_2O	0.15			
	100.11			

of minerals is not controlled by anything corresponding to the known order of crystallization used for the fresh cores. Perhaps it would be impossible to establish a proper choice of minerals, as the grains are so small that they might not be identifiable under the microscope.

In the absence of guiding experience, the process used as is follows:

The phosphorus pentoxide is first taken to make apatite, which incidentally leaves very little lime for future assignment to gypsum, a known constituent of some Hawaiian soils. Next, titania is taken to satisfy the available ferrous oxide for ilmenite, as before, the residue of titania being calculated as rutile. The small amount of manganous oxide is given enough of the large amount of water to form psilomelane. At this stage of the computation the only acids remaining are silica and sulfur trioxide. The sulfur trioxide is then used to make the hydrous sulfates of calcium and magnesium, gypsum, and epsomite. To the small amount of sulfur trioxide remaining is assigned part of the soda for mirabilite, the hydrous sulfate of sodium. Now only silica remains of the acids. To the potash and the remaining soda are assigned proper amounts of the ample silica and alumina to make the feldspars, orthoclase,

and plagioclase. (No lime is available for making more stable minerals.) There now remain only water, ferric oxide, alumina, and silica. To the ferric oxide is given enough water to make limonite. The remaining water is used to make gibbsite, the more hydrous, and bauxite, the less hydrous, both of which are hydrous oxides of aluminum. Finally, the remaining silica is computed as quartz.

TABLE 6

Calculation of the mineral composition of the weathered shells

RADICAL	PER CENT	RADICAL RATIO	Ap.	Il.	Ru.	Ps.	Gy.	Ep.	Mi.	Or.	Ab.	Li.	Ba.	Gi.	Qz.
SiO_2	25.77	4,292	..	...	..	..	.	...	...	198	168	.....	.....	...	3,926
Al_2O_3	34.90	3,423	..	...	..	..	.	...	...	33	28	.....	3,039	323	.....
Fe_2O_3	14.49	908	..	...	..	..	.	...	...	...	...	908	.....	...	.....
FeO	2.77	386	..	386	...	..	.	...	...	...	...	.....	.....	...	.....
MnO	0.18	25	..	...	..	25	.	...	...	...	...	.....	.....	...	.....
MgO	0.14	35	..	...	..	..	.	35	...	...	...	.....	.....	...	.....
CaO	0.24	43	42	...	..	..	1	...	...	...	...	.....	.....	...	.....
K_2O	0.31	33	..	...	..	..	.	...	...	33	...	.....	.....	...	.....
Na_2O	0.44	71	..	...	..	..	.	...	43	...	28	.....	.....	...	.....
SO_3	0.63	78	..	...	..	..	.	35	43	...	...	.....	.....	...	.....
P_2O_5	0.20	14	14	...	..	..	.	...	...	...	...	.....	.....	...	.....
TiO_2	3.47	433	..	386	47	..	.	...	...	...	...	.....	.....	...	.....
H_2O	16.46	9,136	..	...	..	50	2	245	430	...	...	1,362	6,078	969	.....

MINERAL	COMPOSITION	NUMBER OF MOLECULES	MOLECULAR WEIGHT	PER CENT
Apatite	$Ca_3P_2O_8 + 1/3CaF_2$	14	336.34	0.47
Ilmenite	$FeTiO_3$	386	151.94	5.86
Rutile	TiO_2	47	80.1	0.38
Psilomelane	H_4MnO_5	25	138.962	0.35
Gypsum	$CaSO_4 \cdot 2H_2O$	1	172.86	0.02
Epsomite	$MgSO_4 \cdot 7H_2O$	35	246.496	0.86
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	43	322.204	1.39
Orthoclase	$KAlSi_3O_8$*	33	556.49	1.84
Albite	$NaAlSi_3O_8$*	28	524.28	1.47
Limonite	$2Fe_2O_3 \cdot 3H_2O$†	908	186.704	16.95
Bauxite	$Al_2O_3 \cdot 2H_2O$	3,039	137.972	41.93
Gibbsite	$Al_2O_3 \cdot 3H_2O$	323	155.988	5.04
Quartz	SiO_2	3,926	60.06	23.58
				100.14

* These formulas give half the molecular weight used in the upper part of the table.

† This formula gives double the molecular weight used in the upper part of the table.

The abundance of the various minerals in the fresh rock and in the weathered shells is given in table 7.

Comparison of the last column (GG) with the first column (EE) shows that the removal of material by solution has been the chief process in action. This

TABLE 7

Comparison of the mineral compositions of the fresh cores and of the weathered shells

GROUP	MINERAL*	EE	FF	GG
		per cent	*per cent*	*per cent*
Baseless mineral	Quartz	11.56	23.58	9.43
Titania minerals	Ilmenite	5.29	5.86	2.34
	Rutile	.....	0.38	0.15
Potash mineral	Orthoclase	5.23	1.84	0.74
Soda minerals	Noselite	4.05	.....	.....
	Albite	13.11	1.47	0.59
	Mirabilite	.....	1.39	0.56
Lime minerals	Apatite	0.61	0.47	0.19
	Anorthite	25.34	.....	.....
	Wollastonite	8.40	.....	.....
	Gypsum	.....	0.02	0.01
Magnesia minerals	Clinoenstatite	14.82	.....	.....
	Epsomite	.....	0.86	0.34
Iron minerals	Iron metasilicate	4.75	.....	.....
	Magnetite	4.93	.....	.....
	Limonite	.....	16.95	6.78
	Ilmenite†			
Aluminum minerals	Feldspars‡			
	Gibbsite	.....	5.04	2.02
	Bauxite	.....	41.93	16.77
Manganese minerals	Rhodonite	1.07	.....	.....
	Psilomelane	.....	0.35	0.14
	Water	0.89	.....	.....
		100.05	100.14	40.06

* This column groups together minerals with the same bases.

† Ilmenite is also a titania mineral and is listed above.

‡ The feldspars (orthoclase, albite, and anorthite) are listed above with the potash, soda, and lime minerals.

EE—Mineral composition of the fresh rock. The data of the last column of table 4, but in different order.

FF—Mineral composition of the weathered shells. The data of the last column of table 5, but in different order.

GG—Mineral composition of the weathered shells reduced to show the amounts surviving or newly generated. Equals FF $\times \frac{40.06}{110.14}$. This computation assumes no change in alumina.

is shown by inspection for the minerals having titania, potash, soda, lime, magnesia, or manganous oxide as their bases, as well as by the total of all constituents. It is also shown immediately for apatite and quartz. At the first glance it might appear that alumina has been added, but it must be remembered that the alumina in the gibbsite and bauxite is not new alumina, but is derived from the destruction of the three feldspars, orthoclase, albite, and anorthite.

TABLE 8

Parental relationships of original minerals of fresh cores to derived and surviving minerals of weathered shells

PARENT MINERALS	DERIVED AND SURVIVING MINERALS												
	Apatite	Ilmenite	Rutile	Psilomelane	Gypsum	Epsomite	Mirabilite	Orthoclase	Albite	Limonite	Bauxite	Gibbsite	Quartz
Apatite	x	...	...	...	...	...	...	...	...	...	...	...	...
Ilmenite	...	x	x	...	...	...	...	...	...	x	...	...	...
Noselite	...	...	...	...	x	x	x	...	...	...	x	x	x
Orthoclase	...	...	...	...	...	...	...	x	...	...	x	x	x
Albite	...	...	...	...	...	...	x	...	x	...	x	x	x
Anorthite	...	...	...	...	x	...	...	...	...	...	x	x	x
Magnetite	...	...	...	...	...	...	...	...	...	x	...	...	...
Iron metasilicate	...	...	...	...	...	...	...	...	...	x	...	...	x
Wollastonite	...	...	...	...	x	...	...	...	...	...	...	...	x
Clinoenstatite	...	...	...	...	...	x	...	...	...	...	...	...	x
Rhodonite	...	...	...	x	...	...	...	...	...	...	...	...	x
Quartz	...	...	...	...	...	...	...	...	...	...	...	...	x

Table 8 attempts to set forth the genetic relationships of the derived minerals to the parent minerals. Since parenthood cannot be definitely ascribed, only probabilities are indicated, which is done by the use of *X* marks. No further discussion of table 8 seems necessary.

FURTHER EVIDENCE CONCERNING THE TOXIC ACTION OF ALUMINUM IN CONNECTION WITH PLANT GROWTH[1]

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For many years the Rhode Island Agricultural Experiment Station has studied acid-soil conditions. From time to time various aspects of the problem have been explored and the publications of the station show the results of much experimentation. "Active" soil aluminum has been linked with acidity as measured by hydrogen-ion concentration and lime requirement. Much of the work has been based on solution cultures using various plants and amounts of aluminum at different acidities.

Other workers have added to the mass of information now available and two schools of thought have arisen. Line (6) in England has claimed that aluminum cannot exist in the soil solution in sufficient concentration to cause toxicity and that the toxic factor of acid soils is acidity as measured by hydrogen-ion concentration. McLean (8) has shown that aluminum may be toxic to plants in solution culture in amounts far smaller than those found by Line in the soil solutions.

This article describes attempts to clarify the problem by endeavoring to divorce the two factors, acidity and aluminum, and to show by solution culture methods accompanied by the study of certain acid soils from widely separated areas and having differing geological histories, which of the two factors is the more potent.

SOLUTION CULTURES

The indicator plant selected for this work was Cos lettuce. The seedlings were germinated in beach sand and when approximately 1 week old were sorted for uniformity, and placed in corks with their roots immersed. Six plants were placed in each culture and all cultures were in quadruplicate. After 7 days the solution was renewed, and the plants were harvested at the end of 14 days. Colorimetric determinations of pH values were made at the beginning and end of the experiment. The plants were carefully dried in a constant temperature oven, and after they had come to equilibrium with room conditions, air-dry weights were obtained.

[1] Contribution no. 395 of the R. I. Agricultural Experiment Station.

Table 1 gives the ingredients in 1,000 cc. of the culture solutions used in this experiment. Each culture bottle contained 250 cc. of solution.

In table 2 are reported the yields of seedlings grown in the six different culture solutions.

From table 2 it will be noted that although the reactions during the growth period varied from pH 3.2 to 7.5, no appreciable differences in yields are

TABLE 1

Ingredients in 1 liter of culture solutions used with lettuce seedlings

Solution Number		I	II	III	IV	V	VI
	MOLARITY	MODIFIED KNOPS	R. I. SOLUTION B	PFEFFERS' SOLUTION	R. I. SOLUTION A	R. I. SOLUTION A_2 DOUBLED	R. I. SOLUTION A_3 TREBLED
	M	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
$Ca(NO_3)_2 \cdot 4H_2O$	0.100	19	15	40	15	30	45
KH_2PO_4	0.030	8	....	10	..	..	..
$MgSO_4 \cdot 7H_2O$	0.100	8	8	5	8	16	24
$Fe_2(NO_3)_6 \cdot 18H_2O$	0.003	4	4	4	4	8	12
KCl	0.100	..	8	5	8	16	24
$CaH_4(PO_4)_2 \cdot H_2O$	0.010	..	13.6	..	6	12	18
KNO_3	0.100	..	....	10	..	..	..
NH_4NO_3	0.100	..	....	..	10	20	30

TABLE 2

Dry-weight yields of Cos lettuce seedlings grown in nutrient solutions having reaction ranges from pH 3.2 to 7.5

NUTRIENT SOLUTION NUMBER	REACTION RANGE DURING GROWTH PERIOD	DRY-WEIGHT YIELD
	pH	*gm.*
I	5.4–7.5	0.413
II	5.4–7.4	0.447
III	5.2–7.3	0.406
IV	5.3–3.4	0.488
V	5.4–3.4	0.428
VI	5.3–3.2	0.506

noticeable. It would thus appear that in solution Cos lettuce seedlings are not very susceptible to injury from acidity as measured by reaction *per se*.

In order to link the preceding experiment with the effect of aluminum when added to the culture solution Cos lettuce seedlings were grown in solution. The check solution was the same as no. IV (table 1) except that no phosphoric acid was added. Sulfuric acid was added to this culture solution to cause a pH of 4.6 and this constituted the second solution. The third solution con-

sisted of the check solution with the addition of 28 p.p.m. of aluminum as aluminum sulfate.

The alternating solution method adopted by McLean and Gilbert (9) was used. The following alternations were made.

DATE	CULTURE
May 11	I R. I. Solution A but no P_2O_5
	II R. I. Solution A and H_2SO_4 but no P_2O_5
	III R. I. Solution A and $Al_2(SO_4)_3$ but no P_2O_5
May 14	R. I. Solution A with all cultures
May 18	Similar to May 11
May 22	Similar to May 14

Table 3, in which the average yields of lettuce resulting from the aforementioned three treatments are given, shows that with a reaction range of pH 5.3 to 3.6, induced either naturally by selective withdrawal of ions from solution by the plants or artifically by sulfuric acid, no material difference in yield is noted. The addition of 28 p.p.m. of aluminum, however, produced a distinct depression in growth.

TABLE 3

Dry-weight yields of Cos lettuce seedlings as affected by acidity and aluminum

NUTRIENT SOLUTIONS	REACTION RANGE	DRY-WEIGHT YIELD
	pH	*gm.*
R. I. Solution A*	5.3–3.6	0.940
R. I. Solution + H_2SO_4	4.6–3.7	0.901
R. I. Solution + $Al_2(SO_4)_3$	4.6–4.6	0.602

* No phosphoric acid was added to this solution during one-half of the alternations.

ACID SOILS

This portion of the work may well be considered an extension of work begun by Burgess (3) in 1923 to compare "active" aluminum and hydrogen-ion concentration of widely separated acid soils. Samples of acid soils were obtained from widely separated locations. In many cases these were duplicates of the soils used by Burgess. Reference is, therefore, made to the aforementioned publication for their description. In some cases it would seem that during the interval between Burgess' work and the obtaining of the 1928 samples some of the fields from which these samples were taken had received lime.

Certain of the soils used in this work and which were not described in the 1923 publication are listed in the following:

RHODE ISLAND.—*Merrimac Silt loam.* This soil was taken from plat 82 of the area devoted to field experiments at the Rhode Island Agricultural Experiment Station. This plat has been well fertilized for many years but has received no lime.

CONNECTICUT.—*Taugwank loam.* This sample was taken from an old mowing lot near Stonington. It has not been fertilized or manured for many years.

Hollis Silt loam. This soil was obtained from an old mowing lot near Woodbridge. No fertilizer or manure had been applied for 18 years.

ILLINOIS.—*Muscatine Silt loam.* This sample was taken in Champaign County. It is a friable medium-brown silt loam.

NEW JERSEY.—*Sassafras Silt loam.* This sample was taken from the college farm at New Brunswick. It is a sedentary soil and is derived from unconsolidated deposits of sand, gravel, and clay.

The chemical determinations,[2] the results of which are reported in table 4, were made according to proved and common methods. Soil reactions were determined by the quinhydrone electrode. The lime requirements were determined by the Jones calcium acetate method as described by Burgess (1), except that the results were calculated to the dry soil basis and that soil particles that failed to pass a 2-mm. sieve were discarded. "Active" aluminum as defined by Burgess (2) is that dissolved from 1 part of soil shaken for 1 hour with 5 parts of 0.5 *N* acetic acid. The samples used for this extraction were passed through a 5-mesh sieve. Aluminum in the extract was determined by a procedure based on the method recommended by Lundell and Hoffman (7). The results were calculated to the dry soil basis.

Manganese soluble in 0.5 *N* acetic acid was determined for all soils as recommended by Jacobson,[3] but since the greatest concentration found, 70 p.p.m. of dry soil, is considered too low to indicate manganese toxicity, the results were not included in the tabulation.

At the beginning of the physiological work, lettuce seedlings were chosen as being sensitive to soil acidity and "active" aluminum. Burgess and Pember (4) have shown lettuce to be very sensitive when grown in soil, and McLean and Gilbert (8) have placed the limits at which aluminum in solution was toxic to lettuce as 2 p.p.m. of added aluminum. Lettuce was grown in these soils, but was found too sensitive for the purpose. The dry weights were so small that they were not considered worthy of inclusion in this report. In fact with several of the soils no growth took place after the lettuce plants were set in the pots.

Thus it became necessary to choose a crop less sensitive, and, following the classification given by Burgess and Pember (4) of "comparative resistances of certain plants to soil acidity and active aluminum," barley was chosen. This crop proved to be more suitable.

For this study Wagner pots were used and approximately 6,000 gm. of dry soil was weighed into each pot. Each soil was studied in duplicate. The water-holding capacity of the soils was determined and the moisture made up to 60 per cent of this figure. After the soils had stood for 14 days in the moist state, a 200-gm. sample was taken for chemical determination from each

[2] The chemical determinations were made by John B. Smith, chemist.

[3] Correspondence with H. G. M. Jacobson, Connecticut Agricultural Experiment Station.

pot. Previous to the planting of the lettuce 7.5 gm. $CaSO_4$, 1 gm. $Ca(NO_3)_2 \cdot 4H_2O$, and 0.5 gm. K_2SO_4 were mixed with the soil in each pot. Once during the growth of the lettuce, 1 gm. of $NaNO_3$ was applied to each pot in solution.

After the lettuce was harvested, the soil was removed from each pot and remixed. Then 1 gm. $Ca(NO_3)_2 \cdot 4H_2O$ and 0.5 gm. K_2SO_4 were mixed with the soil from each pot. During the growth of the barley 1 gm. $NaNO_3$ and 0.5 gm. K_2SO_4 were added. The barley seed was planted May 18, 1929, and

TABLE 4

Chemical determinations and dry-weight yields of barley from acid soils

LOCATION	SOIL TYPE	REACTION		JONES CaO REQUIREMENT FOR 2,000,000 POUNDS SOIL	ACTIVE Al_2O_3 IN DRY SOIL	P_2O_5 CONTENT OF BARLEY (DRY MATTER BASIS)	RELATIVE YIELD OF BARLEY
		pH	Wherry's scale active acidity				
				pounds	*p.p.m.*	*per cent*	
Group I:							
Indiana	Clermont silt loam	4.58	250	2,817	81	0.328	8.5
Rhode Island	Merrimac silt loam	4.71	200	2,907	840	0.636	100.0
Connecticut	Taugwank loam	4.75	160	3,645	905	0.324	16.0
New Jersey	Sassafras silt loam	4.83	160	2,502	494	0.464	10.2
Pennsylvania	De Kalb silt loam	4.90	125	2,646	428	0.133	6.8
Group II:							
Indiana	Scottsburg silt loam	5.04	100	4,509	67	0.405	144.0
South Carolina	Portsmouth sandy loam	5.07	80	3,168	117	0.498	176.2
Pennsylvania	Volusia silt loam	5.08	80	3,006	260	0.335	83.0
Connecticut	Hollis silt loam	5.18	63	2,925	519	0.409	132.0
Illinois	Muscatine silt loam	5.48	32	2,655	31	0.317	179.6
North Dakota	Fargo clay	5.76	16	2,250	Trace	0.483	137.3
Maine	Silt loam	5.83	16	1,512	589	0.344	13.5
Group III:							
Texas	Lufkin fine sandy loam	6.20	...	567	41	0.494	54.2
South Carolina	Greenville clay loam	7.01	...	261	79	0.552	81.3
Iowa	Carrington loam	7.25	...	270	18	0.509	120.3
Kentucky	Memphis silt loam	8.12	...	180	53	0.317	94.9

harvested when the heads were yellow on August 12, 1929. Dry-weight yields are shown in table 4.

It will be noted that no phosphoric acid was added to the soils during the growth experiment. This was because of the known effect (4) of phosphatic fertilizers in rendering aluminum non-toxic.

DISCUSSION

For ease in discussion of table 4, the data have been divided into three groups, arbitrarily, according to the reactions of the various soils. Group I

contains those soils with reactions below pH 5; group II is intermediate and less acid in reaction, containing those soils in the range of pH 5.04 to 5.83; whereas in group III are soils which are but slightly acid, having reactions above pH 6. Soils of group III will not be considered in this discussion. Relative barley yields are reported on the basis of Rhode Island station plat 82 as 100. The actual yield for this soil was 29.5 gm.

In order to obtain some measure of the possible effect of soil phosphorus on the growth of barley the crop was analyzed and the P_2O_5 reported on the dry-matter basis. It has been noted that where P_2O_5 is known to be high through fertilizer application it may be expected to show in increased amounts in the crop.

Group I

The dry-weight yields of barley from soils of group I are low, whereas the amounts of "active" aluminum present in dry soil and soluble in 0.5 *N* acetic acid are high. Exceptions to this statement are noted with barley on the Merrimac silt loam and with the aluminum in the case of the Clermont silt loam. The phosphoric acid content of the barley grown on this soil indicates that sufficient phosphoric acid may have been present, as a result of fertilization, so that to some extent the toxic effect of the aluminum was counteracted, and the growth of barley was inhibited to a lesser degree than on the other soils of this group.

The depression of barley on the Indiana soil may have been due to other inhibiting factors than aluminum or acidity. This soil described by Conner et al (5) as "a white, flat, timber soil, very low in organic matter and nitrogen." In addition to these deficiencies the tilth of this soil was found to be poor and the soil was inclined to puddle when an attempt was made to leach it.

If the Clermont silt loam soil is disregarded, the four soils remaining in group I indicate that either the aluminum or the reaction acidity was an inhibiting factor in the growth of barley, as both seem to correlate with the low relative dry-weight yields.

Group II

Since the reaction range of soils in Group II is between pH 5.04 and 5.83 and the dry-weight yields of barley vary from 13.5 to 179.6 gm. and are not consistent in their variation, no correlation seems to exist with reaction acidity. On the other hand if each soil be considered separately and the relative yield checked with the amount of "active" aluminum in the soil, in all cases, except that of the Hollis silt loam, where the aluminum is high, the relative dry weight is low and *vice versa*. The only reason for this discrepancy with the Connecticut soil may be found in the somewhat higher content of phosphoric acid in the barley, which may reflect a tying-up of aluminum in the soil. This, however, is only suggestive. With the Maine soil, even with a reaction which

can hardly be considered as very acid, sufficient aluminum seems to have been present to depress the barley very seriously.

It is thus necessary to turn to the intermediate group II for a suggestion as to the inhibiting factor. Group I, possibly because of the genesis of the soils in that group, which Burgess offers as a reason for the correlation which he found between acidity and aluminum content, does not allow the separation of the factors depressing the barley crop. Group II, however, where the acidity range is much less and where a greater variation in soil genesis is found as a result of the wider geographical spread in locations from which the samples were obtained, points quite definitely to the "active" aluminum content as the limiting factor in the growth of barley.

SUMMARY

In this paper further evidence is offered indicating that in soil and solution cultures "active" aluminum has a greater inhibitory effect on the growth of lettuce and barley plants than has acidity.

Solution cultures of Cos lettuce seedlings grown in a pH range of 3.2 to 7.5 showed no appreciable differences in dry-weight yields although cultures to which aluminum sulfate had been added were much depressed in yield.

The dry-weight yields of barley plants grown in samples of acid soils from several different soil types and widely separated geographically, were more closely correlated with the "active" aluminum content of the soils than with acidity.

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A SIMPLE METHOD OF ESTIMATING TOTAL EXCHANGEABLE BASES IN SOILS

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Bases in soils exist in two forms: Free as carbonates, or combined with the colloidal complex. The latter are sometimes spoken of as "absorbtively bound" or exchangeable bases. They are determined by leaching the soil with a neutral salt solution like ammonium chloride (4), barium chloride (1), or sodium chloride (3); or with a dilute acid like 0.05 *N* HCl (2). Also by electrodialysis (5), or electrofiltration (6).

None of these methods, however, is free from objection, as a certain amount of free carbonates are bound to appear in the leachate; and the success of a method must inevitably rest on the prevention of carbonate dissolution. In Hissink's method (3), the soil is washed in two lots; the amount of calcium in the second lot is supposed to represent the quantity dissolved, and subtracting it from that in the first lot gives the exchangeable calcium. In the neutral salt displacement method, the soluble salts also appear with the exchangeable bases and introduce a corresponding error.

The evaluation of total exchangeable bases, would be of great importance in any system of genetic classification of soils. For routine work, however, a rapid and fairly accurate method that can be carried out with the minimum of equipment is needed. It is the object of this paper to outline such a method.

The method consists in the determination of carbonates (representing free bases), as well as total bases (free and exchangeable). The difference between the two values represents exchangeable bases.

DETERMINATION OF CARBONATES

Carbonates are determined by the titration method developed by the author and discussed elsewhere (7). The following is the outline of the method:

Ten grams of soil is stirred with 100 cc. of water in a conical flask and excess $CaSO_4$ (0.2 to 0.5 gm.) added. The mixture is brought to the boiling point over a sand bath or Rose burner. Then 10 cc. of 0.1 *N* Al_2Cl_6 solution is added and the suspension shaken a little. About 10 drops of Brom thymol blue indicator (1 per cent solution in 50 per cent alcohol) is added and the suspension allowed to settle after a vigorous shaking. The soil settles down in several minutes, when the color of the supernatant liquid is noted. Yellow indicates less than 1 per cent carbonates, green to blue indicates more than 1 per cent carbonates. Next, 10 drops of Brom cresol green indicator (1 per cent solution in 50 per cent alcohol) is added and the color again noted. Golden yellow indicates absence of carbonates, green indicates less than 1 per cent

carbonates, deep bluish green indicates more than 1 per cent carbonates. If carbonates are present the procedure is as follows: The flask is brought to the boiling point and the contents are titrated against 0.5 *N* H_2SO_4. The suspension is boiled for a minute or two after each addition and allowed to settle for two minutes. This however, is only necessary in the later stages of titration as it is easy to see the green edge in the beginning. *The titration is complete when the color of the supernatant liquid is golden yellow which persists after the suspension has been boiled for several minutes, and allowed to settle for a minute or two.* The amount of H_2SO_4 used is equivalent to the total carbonates, or free bases in the soil. As a rule 8 to 12 titrations are started at once and completed within several hours.

The method has been shown to give values agreeing with the standard method in which CO_2 is liberated by acid treatment and measured by absorption in baryta. For fuller details the original paper should be consulted.

DETERMINATION OF TOTAL BASES

To 10 gm. of soil contained in a 500-cc. reagent bottle, sufficient 0.5 *N* HCl is added to break up all the carbonates, as determined by the foregoing method. Then 100 cc. of 0.1 *N* HCl is added and the mixture left for a few hours being shaken frequently, till the evolution of CO_2 bubbles has subsided. The bottle is next tightly corked with a rubber bung and mechanically shaken for about two hours. The suspension is filtered through a Büchner funnel, preferably without suction. For this purpose it is necessary to stick the filter paper to the funnel by running a little molten wax around the edges or by applying collodion with a camel's-hair brush. In either case the filter paper should be moistened first, and held on the funnel by suction. The soil on the filter paper is washed with 400 cc. of 0.05 *N* HCl in 100-cc. lots, and then with 200 cc. of water in 100-cc. lots. The filtrate is then made up to a definite volume and an aliquot titrated against standard alkali, phenolphthalein being used as indicator. The decrease in the concentration of the acid used is equivalent to the total bases present.

The quantities of acid solution recommended for washing need not be rigidly adhered to, though they should never be exceeded. For light soils and those containing little or no carbonates, 200 cc. of 0.05 *N* HCl instead of 400 cc. is quite enough. The main point is to wash the soil with an excess of acid (not too strong), till the exchangeable calcium is removed, and determine the amount of acid thus neutralized. The treatment outlined was found to accomplish this even in soils containing more than 50 per cent clay.

DISCUSSION OF RESULTS

In table 1 are given total exchangeable bases for 49 soils determined by the method described. The pH values (by H electrode 1:5 soil-water ratio) and the clay contents of the soils are also recorded. For convenience of reference a column has been added giving the exchangeable bases per gram of clay; these values show a rough correlation with the pH values, and for soils containing an excess of carbonates they give some idea of the base exchange capacity of

TABLE 1

Total bases, carbonates, and exchangeable bases in various soils

SOIL NO. P.C.	CLAY	TOTAL BASES, M.E. PER GM. OF SOIL	CARBONATES, M.E. PER GM. OF SOIL	EXCHANGEABLE BASES, MILLI-EQUIVALENTS PER GM.		pH
				Soil	Clay	
	per cent					
1	11.3	6.964	6.85	0.114	1.01	8.45
2	59.3	1.818	1.00	0.818	1.38	8.21
3	62.2	0.750	0.10	0.650	1.04	7.64
4	15.2	0.366	0.20	0.166	1.09	8.55
5	12.3	0.512	0.374	0.138	1.12	8.77
6	28.4	0.085	Nil	0.085	0.299	5.29
7	21.8	1.468	1.30	0.168	0.77	9.58
8	25.2	0.281	0.15	0.131	0.52	8.41
9	21.6	0.1125	0.024	0.0885	0.41	5.76
10	35.6	0.584	0.225	0.359	1.01	8.71
11	32.8	0.849	0.50	0.349	1.06	8.77
12	7.2	0.075	Nil	0.075	1.04	5.84
13	58.9	0.979	0.30	0.679	1.16	8.53
14	21.5	0.019	Nil	0.019	0.088	5.37
15	22.4	0.125	0.05	0.075	0.33	7.71
16	8.7	0.755	0.374	0.381	4.38	8.74
17	14.1	0.275	0.10	0.175	1.24	8.20
18	22.6	0.083	0.024	0.059	0.26	5.79
19	42.3	0.691	0.20	0.491	1.16	8.40
20	8.1	0.019	0.024	Nil	Nil	5.64
21	13.5	0.834	0.574	0.26	1.93	8.25
22	15.1	0.158	0.024	0.134	0.89	6.85
23	11.3	0.157	0.05	0.107	0.95	7.41
24	9.7	0.598	0.35	0.248	2.56	8.59
25	4.0	0.038	Nil	0.038	0.95	7.40
26	22.5	0.078	Nil	0.078	0.35	8.11
27	53.2	1.508	0.724	0.774	1.45	9.03
28	44.6	0.648	0.174	0.474	1.06	8.38
29	63.0	0.638	0.074	0.564	0.90	8.05
30	54.1	1.398	0.824	0.574	1.06	8.45
31	22.8	0.94	0.804	0.136	0.60	8.01
32	64.6	0.24	0.150	0.09	0.14	5.05
33	2.6	1.175	0.95	0.225	0.87	10.18
34	11.3	0.190	Nil	0.190	1.68	7.63
35	18.3	0.095	0.025	0.07	0.38	7.98
36	11.7	0.18	0.05	0.13	1.11	8.40
37	4.1	0.05	0.025	0.025	0.61	5.72
38	52.9	0.59	0.10	0.49	0.93	8.29
39	8.4	0.51	0.20	0.31	3.69	9.11
40	13.1	0.17	0.024	0.146	1.11	7.65
41	53.4	2.34	1.75	0.59	1.10	8.74
42	53.4	1.905	1.15	0.755	1.41	9.00
43	21.6	1.39	1.124	0.266	1.23	8.41
44	8.4	1.62	1.374	0.246	2.93	8.54
45	11.1	0.09	0.05	0.40	0.36	7.45
46	56.4	0.66	0.10	0.56	0.99	7.63
47	17.1	1.44	1.15	0.29	1.70	9.98
48	19.8	1.41	1.25	0.16	0.81	8.55
49	23.3	0.095	0.05	0.045	0.19	6.33

colloids, for such soils may be considered as saturated with bases in the sense that any excess added would be converted into carbonates.

That the determination of exchangeable bases by neutral salt reaction can be very misleading, is shown by the following experiment in which a heavy black cotton soil (P.C.2) was leached with *N* and 0.2 *N* NH_4Cl, and with 0.1 *N* $BaCl_2$ solution, in 100-cc. lots. Ca was determined in 400-cc. lots of the leachate. The results are recorded in table 2.

Table 2 shows that NH_4Cl solution is not a suitable reagent for determining exchangeable bases; $BaCl_2$ solution on account of the limited solubility of $CaCO_3$ in it seems to be much superior (1). Considering that leaching with $BaCl_2$ solution was not carried beyond 1,200 cc., and bearing in mind that only Ca was determined in the leachate, the auther's method may be taken as comparable to $BaCl_2$ washing.

TABLE 2

Removal of Ca from soil P.C.2 in successive washings with NH_4Cl and $BaCl_2$ solutions

SUCCESSIVE 400-CC. WASHINGS	M.E. OF Ca FROM 10 GM. OF SOIL			TOTAL EXCHANGEABLE BASES BY THE AUTHOR'S METHOD, M.E. PER 10 GM. OF SOIL
	N NH_4Cl	0.2 *N* NH_4Cl	0.1 *N* $BaCl_2$	
1	8.8	7.0	5.6	....
2	2.825	2.84	0.38	....
3	1.11	1.6	0.48	....
4	1.96	0.95	....	....
5	1.21	0.91	....	....
6	0.165	....	....	....
Total.....	16.07	13.30	6.44	8.18

SUMMARY

A method for the estimation of total exchangeable bases in soils is outlined. It consists in the determination of carbonates by the author's titration method, and of total bases by dilute HCl treatment; the difference between the two values giving the exchangeable bases.

The results of such determinations on 49 soils from different parts of India are recorded.

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SAMPLING MARKET-GARDEN SOILS FOR NITRATES[1]

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In anticipation of a growing need for knowledge regarding methods for chemical control of available soil nitrogen during the growth of crops, especially of market-garden vegetables, a study has been made of the distribution of soil nitrates under the heterogeneity that exists in such conditions, with a view to deciding upon a sampling scheme. In a strict sense the data have only a local application, but publication of the results supplements the findings of Waynick (4) and Prince (3) who studied more uniform conditions, and may aid those who wish to work with drilled vegetable crops growing in highly-manured soils, fertilized with hand-distributed chemicals, and further supplemented from time to time with side-dressings of soluble nitrogen.

EXPERIMENTAL PROCEDURE

Soil

The areas selected were three $\frac{1}{80}$-acre plats of a market-garden rotation (*W*) last described by Hartwell and Crandall (2). The soil has been classified as Merrimac silt loam. Since 1916, these plats have received considerable quantities of stable manure, for which a mixture of manure with vegetable compost has been substituted recently. The manure applied in the spring has been supplemented liberally by complete inorganic fertilizers, both in the spring and before the second crops that are planted at midseason. Sufficient lime has been used to maintain a neutral reaction. The initial application of fertilizer for the crops studied was sown broadcast by hand, but certain of the early crops that preceded these were fertilized in the hill, and all crops have had side-dressings of soluble nitrogen at various times in the growing season. Thus, the original uniformity of the soil has been disturbed by the unevenness unavoidable in distributing fertilizer by hand, hill fertilization in a few instances, the application of soluble nitrogen between the rows of the growing crops, and variable absorption by the crops.

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Sampling and analysis

The samples were taken during September and October, 1928, after the harvest of the early crops and while beets, celery, and spinach were growing. Eight borings were taken from each of five rows extending lengthwise of a rectangular plat, and within 6 inches of the crop row. The rows selected were approximately 4 feet apart and the borings were spaced 5 feet apart in the row. The borings are not numbered in the tables presented, but the location of each individual result in the table corresponds to its location on the rectangular plat. Thus, the tables represent sampling diagrams as well as records of the data.

Each sample consisted of a single core, 0.75 inches in diameter, taken with a "trier" to a depth of 7 inches. The samples were brought to the laboratory, passed through a 5-mesh sieve, and portions for analysis were weighed immediately. Nitrate nitrogen was determined by the phenoldisulfonic acid method as modified by Harper (1). All results were corrected to a dry soil basis by using a uniform correction factor for each set of borings. The factor was calculated from the mean of the moisture determinations for 10 cores well distributed over the area. Preliminary moisture determinations in a larger number of borings showed small variations and it was calculated that the probable error of the mean of 10 determinations was less than 0.5 per cent of that mean.

The accuracy of the laboratory method for nitrate nitrogen was checked by determinations in 28 duplicate portions of soil. The greatest variation noted was 1 p.p.m. of nitrate nitrogen in dry soil. As this is the smallest difference that could be shown between two colorimeter readings in the dilutions of extract that were used, the actual variations were less than this value. It is recognized that there is a laboratory error that varies in magnitude with the concentration of nitrates in the solution analyzed, but it is small in comparison with the sampling error and has been disregarded.

Statistical methods[2]

The customary formulas for standard deviation (σ) and probable error of the mean (PE_m) were used.

$$\sigma = \sqrt{\frac{\Sigma d^2}{N-1}} \qquad PE_m = \frac{0.6745\,\sigma}{\sqrt{N}}$$

In the formula for σ, $N-1$ was used in the denominator rather than N for greater accuracy in dealing with small groups of data. The application of these formulas to soil-nitrate studies has been discussed fully by Waynick (4) and Prince (3). For comparison of the nitrate uniformity under different soil and

[2] The authors are indebted to Dr. T. E. Odland for suggestions as to the use of statistical formulas.

crop conditions the errors have been calculated as the percentage ratios of the errors to their means $\left(\frac{100\ PE_m}{M}\right)$. Thus, for a soil containing 20 p.p.m. of nitrate nitrogen, a PE_m of 5 per cent signifies that the chances are even that the true mean lies between 20 ± 1 p.p.m., and about 30 to 1 that it lies within 3 PE_m, or between 17 and 23 p.p.m. in this instance.

The statistical methods employed are applicable only to data that are distributed uniformly about the mean. Although this uniformity can usually be assumed, it seemed desirable to test the assumption in this instance. For this purpose nitrate nitrogen was determined in 95 borings taken from a $\frac{1}{80}$-acre plat. The results were grouped in classes with limits 5 p.p.m. apart (table 3). Although a line connecting the midpoints of the upper sides of the rectangles of the histogram charted from these data was somewhat asymmetrical, the mean fell very close to the midpoint of the modal class, and it seems reasonable to assume that the lack of symmetry is caused by a dearth of data rather than by a true lack of uniformity in distribution. The evidence of normal distribution of results about the mean was accepted as satisfactory.

To show the reliability of composites of different numbers of borings, the constants have been calculated for various combinations of the individual results as well as for the whole number taken from each plat. Each group of 20, 13, and 6 results is made up from borings spaced as uniformly as possible over the plat and no result was used twice in groups of the same size.

At the outset, a probable error of 5 per cent of the mean was chosen as the maximum allowable variation and the data have been studied with this in mind.

DISCUSSION OF RESULTS

The data reported in tables 1, 2, and 3 were obtained from a plat planted to spinach September 5. The early tomatoes that preceded the spinach had received 60 pounds[3] of nitrogen applied close to the plants. A mixture of nitrate of soda and sulfate of ammonia sufficient to supply 20 pounds of nitrogen was broadcast and harrowed in when the spinach was planted, followed by a side-dressing of 30 pounds on October 4. At the first sampling date, September 18, the plants were still in the cotyledon stage and could not have affected samples taken midway between the rows. This set of results has been labelled "fallow" (table 1). The second set of samples was taken a month later, 2 weeks after the application of the side-dressing, and when the crop was one-quarter grown. The borings were taken within 6 inches of the row (table 2). A third set, containing 95 borings, was taken October 23 after the plants were more than half grown. To save space, only a statistical summary of the 95 borings is recorded in table 3. The data were grouped in classes for the construction of the distribution diagram already mentioned,

[3] All applications are reported on the acre basis.

but the statistical constants were calculated from the individual determinations.

The quantities of nitrate nitrogen were within the normal range and decreased from 41.7 p.p.m. in the fallow to 35.7 p.p.m., when the crop was quarter grown, and to 13 p.p.m. at the last sampling date. The probable errors calculated as percentages of the means based on approximately 40 borings increased for the last sampling as compared with the first two, but the general uniformity was greater than for the other crops studied. There was a decided increase in the probable error for composites of less than 40 borings, and the error was usually greater than 5 per cent when less than 20 borings were considered. There is a noticeable lack of uniformity among the different groups of less than 20 borings.

TABLE 1

Nitrate nitrogen in fallow, September 18, 1928—Plat 115

Individual borings, p.p.m. of NO_3-N in dry soil

25	25	25	35	35	29	51	58
58	35	19	58	41	82	19	62
37	..	33	45	62	58	53	41
53	49	33	33	33	26	27	41
37	29	41	58	49	41	33	58

Statistical summary

39 BORINGS		20 BORINGS*		13 BORINGS*		6 BORINGS*	
M PE$_m$	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*
41.7 ±1.5	4	38.2 ±1.9	5	42.5 ±1.8	4	42.0 ±2.6	6
.....	..	†45.4 ±2.3	5	42.0 ±3.4	8	49.5 ±5.9	12
.....	..	.....	..	40.7 ±2.8	7	37.0 ±4.7	13
.....	..	.....	..	.....	..	43.2 ±3.2	7
.....	..	.....	..	.....	..	36.2 ±3.7	10
.....	..	.....	..	.....	..	41.5 ±3.7	9

* The results are combined so that each group of borings is distributed over the area with equal uniformity.

† Nineteen borings.

Two sets of samples were taken under beets; the first on September 5, five weeks after the crop was planted, and the second October 9, when the plants were full grown. Liberal quantities of nitrogen were applied broadcast and in side-dressings for the cabbage that preceded the beets. The data are reported in tables 4 and 5. Seventy-five pounds of nitrogen in nitrate of soda and sulfate of ammonia were applied in three equal applications, the first as a broadcast at planting time, the second and third as side-dressings on September 21 and October 3. The plat is manured twice in each 3-year period but not in the cabbage-beet year.

TABLE 2

Nitrate nitrogen under small spinach, October 18, 1928—Plat 115

Individual borings, p.p.m. of NO_3-N in dry soil

27	33	23	71	39	31	31	33
31	27	33	23	19	39	37	41
27	21	17	27	27	50	35	35
44	46	54	50	56	33	37	37
37	29	33	48	37	33	31	46

Statistical summary

40 BORINGS		20 BORINGS*		13 BORINGS*		6 BORINGS*	
M PE$_m$	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*
35.7 ±1.2	3	34.0 ±1.5	4	36.9 ±2.7	7	29.2 ±2.9	10
.....	..	38.0 ±1.8	5	36.2 ±1.5	4	35.8 ±1.8	5
.....	..	.....	..	33.2 ±1.8	5	34.8 ±3.0	9
.....	..	.....	..	.....	..	44.7 ±4.5	11
.....	..	.....	..	.....	..	37.2 ±2.8	8
.....	..	.....	..	.....	..	31.8 ±2.7	8

* The results are combined so that each group of borings is distributed over the area with equal uniformity.

TABLE 3

Nitrate nitrogen under half-grown spinach, October 23, 1928—Plat 115, 95 borings

NO_3-N, p.p.m.....	0–5	5. 1–10	10. 1–15	15. 1–20	20. 1–25	25. 1–30	30. 1–35	35. 1–40
Number of borings.....	13	24	29	19	5	2	2	1

Statistical summary

Calculated from individual determinations of NO_3-N in p.p.m

95 BORINGS*		48 BORINGS*		19 BORINGS*		12 BORINGS*		6 BORINGS*	
M PE$_m$	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*	*M PE$_m$*	*per cent*
13.0 ±0.5	4	12.5 ±0.7	6	14.0 ±1.0	7	12.1 ±1.3	11	13.2 ±0.8	6
.....	..	13.5 ±0.6	4	11.6 ±1.0	9	14.9 ±1.5	10	9.8 ±2.1	21
.....	..	.....	..	13.6 ±0.8	6	13.8 ±1.6	12	13.2 ±1.6	12
.....	..	.....	..	14.9 ±1.4	9	12.2 ±0.9	7	12.2 ±1.1	9
.....	..	.....	..	11.7 ±1.2	10	12.1 ±1.5	12	10.2 ±0.8	8
.....	..	.....	..	.....	..	15.7 ±1.7	11	15.7 ±2.7	17
.....	..	.....	..	.....	..	12.1 ±1.0	8	13.3 ±2.9	22
.....	..	.....	..	.....	..	.....	..	10.7 ±1.5	14
.....	..	.....	..	.....	..	.....	..	10.3 ±1.5	15
.....	..	.....	..	.....	..	.....	..	17.2 ±3.2	19

* The results are combined so that each group of borings is distributed over the area with equal uniformity.

On September 5 there were 29.9 p.p.m. of nitrate nitrogen under the half-grown beets but despite the two side-dressings, the concentration was reduced to 4 p.p.m. by October 9 when the crop was ready for harvest. The 4 p.p.m.

TABLE 4

Nitrate nitrogen under half-grown beets, September 5, 1928—Plat 112

Individual borings, p.p.m. of NO_3-N in dry soil

28	30	24	30	32	22	24	51
67	36	22	36	42	28	63	71
32	26	32	30	..	34	32	34
42	32	32	32	32	34	47	38
4	7	6	6	3	10	10	6

Statistical summary

39 BORINGS		20 BORINGS*		13 BORINGS*		6 BORINGS*	
M PE_m	*per cent*	*M* PE_m	*per cent*	*M* PE_m	*per cent*	*M* PE_m	*per cent*
29.9 ±1.8	6	†30.2 ±2.7	9	31.8 ±2.9	9	32.7 ±1.8	6
.....	..	30.0 ±2.4	8	26.5 ±2.4	9	29.2 ±4.1	14
.....	..	.....	..	32.0 ±3.8	10	37.8 ±6.4	17
.....	..	.....	..	.....	..	34.5 ±5.8	17
.....	..	.....	..	.....	..	26.7 ±3.1	12
.....	..	.....	..	.....	..	29.3 ±4.4	15

* The results are combined so that each group of borings is distributed over the area with equal uniformity.

† Nineteen borings.

TABLE 5

Nitrate nitrogen under full-grown beets, October 9, 1928—Plat 112

Individual borings, p.p.m. of NO_3-N in dry soil

2.8	2.8	2.6	2.4	3.8	4.8	5.1	9.2
2.6	2.6	2.8	7.0	3.2	3.6	7.4	4.6
3.8	3.4	2.8	7.6	7.2	8.8	5.0	6.6
4.6	1.6	1.2	12.0	1.6	2.0	3.8	1.4
2.4	1.2	1.6	1.4	2.4	2.4	7.0	4.6

Mean of 40 borings 4.09±0.28

$$\frac{PE_m \times 100}{M} = 7 \text{ per cent}$$

level was so low that the accuracy of the laboratory method scarcely justifies calculation of the statistical constants. By extending the calculations somewhat beyond the exact accuracy of the determinations, however, a value for the probable error was found and is reported in table 5. No great reliance

should be placed in this constant, but it is evident that the variation is high. The probable error is also high for the half-grown beets, 6 per cent, where 39 borings were taken, and much greater for composites of lesser numbers of borings. The nitrogen in the borings from just inside the outer row of beets represented by the lower line of results in table 4, is much less than that from the remainder of the plat, demonstrating a lack of uniformity in fertilizer distribution.

Samples were taken under half-grown celery on September 14 (table 6). This crop was preceded by lettuce. A heavy application of manure compost was used in the spring and liberal quantities of fertilizer nitrogen were broadcast for the lettuce. Celery plants were set in July but no nitrogen or potash

TABLE 6

Nitrate nitrogen under half-grown celery, September 14, 1928—Plat 118

Individual borings, p.p.m. of NO_3-N in dry soil

16	27	37	41	29	16	16	62
23	12	12	8	41	51	41	25
47	33	12	51	31	23	25	10
7	14	3	9	6	18	6	16
10	25	18	8	8	33	41	70

Statistical summary

40 BORINGS		20 BORINGS*		13 BORINGS*		6 BORINGS*	
M PE_m	*per cent*	*M* PE_m	*per cent*	*M* PE_m	*per cent*	*M* PE_m	*per cent*
24.5 ±1.7	7	21.5 ±2.1	10	18.5 ±2.2	12	16.3 ±3.5	21
.....	..	27.6 ±2.8	10	30.1 ±3.3	11	36.8 ±5.6	15
.....	..	.....	..	21.5 ±2.6	12	24.2 ±4.2	17
.....	..	.....	..	.....	..	22.5 ±3.1	14
.....	..	.....	..	.....	..	22.8 ±4.0	18
.....	..	.....	..	.....	..	15.5 ±2.6	17

* The results are combined so that each group of borings is distributed over the area with equal uniformity.

was used until August 10 to avoid high concentrations of soluble salts about the tender plants in rather dry soil. On August 10, 25 pounds of nitrogen in a mixture of nitrate of soda and sulfate of ammonia was applied as a side-dressing and again on August 31. The plants available on July 12 were only sufficient to set five rows and the remaining two were filled in July 25. Nitrate determinations from borings beside the two rows of younger plants are reported in the top line of table 6. The shorter feeding time was reflected in a slightly higher average for nitrate nitrogen than that for the remainder of the data. A greater variation is evidenced, however, in the fourth line of results, which are less than half the average for borings in the other rows. This discrepancy is ascribed to uneven distribution of the side dressings.

This set of results represents the extreme variability found for this type of cropping, and the 40 borings taken were not sufficient to reduce the error to 5 per cent. Composites of 20 borings or less gave errors of 10 per cent or greater.

A summary of the data (table 7) for the six different soil and crop conditions shows the greatest uniformity for the fallow and for small spinach. As the crops increased in size the errors were larger. For the most favorable condition studied the probable error varied from 3 per cent with 40 borings to 7 per cent as an average for 6 groups of 6 borings. For the least favorable, the probable errors increased from 7 per cent for 40 borings to 17 per cent for an average of 6 groups of 6 borings. At the best these errors are large, but the increased accuracy from larger numbers of borings is clear.

Apparently for conditions similar to those studied composite samples of 40 borings from $\frac{1}{80}$-acre areas of drilled market-garden crops may be expected

TABLE 7

Summary of probable errors for nitrate nitrogen under growing crops, expressed as the percentage ratios of the probable errors to the respective means of different combinations of data from individual borings

$\frac{1}{80}$ ACRE	BORINGS	PE_m	BORINGS	PE_m*	BORINGS	PE_m†	BORINGS	PE_m‡
	number	*per cent*	*number*	*per cent*	*number*	*per cent*	*number*	*per cent*
Fallow	39	4	20	5	13	6	6	10
Small spinach	40	3	20	5	13	5	6	7
Half-grown spinach	48	5	19	8	12	10	6	14
Half-grown beets	39	6	20	9	13	9	6	14
Full-grown beets	40	7	..	..	..	..	..	..
Half-grown celery	40	7	20	10	13	12	6	17

* Average of two groups of borings.
† Average of three groups of borings.
‡ Average of six groups of borings.

to give errors of approximately 5 per cent; 20 borings, 7 per cent; 13 borings, 8 per cent, and 6 borings, 12 per cent.

COMPARISON OF NITRATE SAMPLING DATA FOR DIFFERENT CROPPING CONDITIONS AND GEOGRAPHICAL LOCATIONS

The data of Waynick (4) for a California fallow, presumably unfertilized and of Prince (3) for timothy sod in New Jersey were compared with the Rhode Island results under vegetables by segregating the data for $\frac{1}{80}$-acre areas measured to scale on the published diagrams of the sampling schemes. The comparison is not strictly accurate since Waynick took borings that were 6 inches in diameter; Prince used composites of three 1-inch borings taken close together to form units; whereas the results in this paper are based on individual cores $\frac{3}{4}$ inch in diameter. The depth was approximately 7 inches in each

case. The larger borings would undoubtedly tend to overcome the lack of uniformity.

The standard deviation (σ) was determined for the greatest number of borings reported for the $\frac{1}{80}$-acre area selected in each case. By substituting this value in the formula for PE_m any number of samples (N) may be assumed and the corresponding theoretical probable error (PE_m) calculated; or a desired PE_m may be substituted in the equation and the number of samples required to give this error may be determined.

TABLE 8

Comparison of the uniformity of soils from widely separated areas, with respect to nitrate nitrogen and the number of borings necessary for an adequate sample

Results are calculated to the basis of $\frac{1}{80}$-acre and probable errors are expressed as per cent of the mean

	NUMBER OF BORINGS USED AS BASIS OF CALCULATION	APPROXIMATE PE_m TO BE EXPECTED FROM COMPOSITE SAMPLES				NUMBER OF BORINGS REQUIRED TO GIVE PROBABLE ERROR OF	
		40 borings	20 borings	13 borings	6 borings	3	5
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Rhode Island:							
Fallow	39	4	5	6	9	59	21
Small spinach	40	3	4	6	8	48	17
Half-grown spinach	48	5	8	10	14	135	49
Half-grown beets	39	6	8	10	15	151	55
Half-grown celery	40	7	10	13	18	225	81
California:*							
Fallow	33	3	4	5	7	34	12
New Jersey:†							
Timothy (manured)	16	3	5	6	9	53	19
Timothy (not fertilized)	16	2	3	4	5	18	7
Timothy ($NaNO_3$)	16	2	3	3	5	18	6

* Calculated from data published by Waynick (4).

† Calculated from data published by Prince (3).

By the use of this method the errors to be expected for nitrate nitrogen in composites of 40, 20, 13, and 6 borings have been calculated for the various soil and crop conditions (table 8). For the larger groups, the values found compare very closely with those obtained by the actual grouping of individual results (table 7), and for the average errors of several smaller combinations of data, but the errors from single composites of 13 or of 6 individuals often vary widely from the average. Great reliance cannot be placed in errors from composites made up of small groups of individuals when these are calculated from the standard deviations of larger groups from similar conditions.

The numbers of borings necessary to limit the errors to 3 per cent and to 5 per cent were calculated and are also presented in table 8.

The most uniform conditions were the unmanured New Jersey plats under timothy, followed by the California fallow and the New Jersey plat with manure. The Rhode Island areas were the least uniform, as would be expected, because of the heavy annual applications of manure compost, hand distribution of large mineral fertilizer supplements, soluble nitrogen top-dressings, and the nitrate removal by growing vegetable crops in drills during the sampling period. Among the different Rhode Island conditions the best uniformity was for a fallow and for small spinach. As the crops became larger the error increased but differences noted among the different crops, spinach beets, and celery, were not sufficient to be ascribed to the specific crops.

The numbers of borings required to give probable errors of 3 per cent for $\frac{1}{80}$-acre areas varied from 18 borings for the unmanured New Jersey plats under the timothy to 225 borings under growing celery in Rhode Island. For 5 per cent errors the corresponding numbers of borings were 6 and 81.

It is evident that each problem should be studied before deciding upon the sampling method, but certain general conditions may be grouped. Apparently fallows and broadcast crops will give probable errors of less than 3 per cent for nitrate nitrogen if 40 borings are taken for $\frac{1}{80}$-acre areas and less than 5 per cent when 25 borings are used. Drilled crops in manured soils supplemented by applications of chemical fertilizer require a minimum of 50 borings to reduce the probable error to approximately 5 per cent, and especially unfavorable conditions may require greater numbers.

SUMMARY

Nitrate nitrogen was determined in 40 cores of soil from manured, limed, and fertilized soils under drilled market-garden crops. Sets of samples were taken from fallow and from under small spinach, half-grown spinach, half-grown and full-grown beets, and half-grown celery. The uniformity of nitrate distribution under these conditions, as shown by the usual statistical constants, was markedly less than that noted by other workers for fallow and for timothy sod. A minimum of 50 borings proved necessary for $\frac{1}{80}$-acre areas of drilled vegetable crops to reduce the probable error for nitrate nitrogen to approximately 5 per cent of the mean.

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THE CONCEPTION OF FLOW-PLASTICITY AS APPLIED TO SOILS

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When a paste of soil[2] or clay in water is caused to flow through a capillary tube at a series of different pressures, the volume of the flow during each second being measured at each pressure, a flow-curve may be obtained by plotting pressure (P) against flow (V), which, it has been shown (5), may be divided into four distinct regions. In the first region of pressure, there is no flow at all, the limiting pressure for this region being a sort of adhesion value, or "yield-value" (1) for the water layer separating the body of paste in the tube from the glass wall. Let this limiting pressure be disignated a.

As soon as a is reached, the body of paste starts to flow as a solid block or plug along the tube, sliding through the water envelope, which remains constant in thickness. This second region of the flow-curve is linear, the straight line hitting the pressure axis sharply at a.

When a second critical pressure, b, is reached, a telescopic type of flow starts at the wall: and as pressure is still further increased, the flow-curve slopes very steeply upwards, as the width of the region of telescopic (or "fluid") flow increases in thickness toward the centre of the tube at the expense of the central plug.

Finally, in the fourth region, the "plug" has virtually disappeared, and the material streams as a fluid, giving a straight-line flow-curve having a slope about a hundred times that of the second region, or plug straight line.

The critical pressures a and b depend on the radius and length of the capillary tube used, but it has been shown that if we set

$$A = \frac{aR}{2L} \quad \text{and} \quad B = \frac{bR}{2L}$$

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[1] The author, who is a staff member of the Rothamsted Experimental Station, Harpenden, England, performed the work reported in this paper, in the Baker Laboratory of Cornell University.

The author wishes to express his thanks to Prof. W. D. Bancroft of Cornell University for much help and many suggestions, to the director and staff of the New Jersey State Agricultural Experiment Station, and especially to Drs. J. S. Joffe and L. L. Lee, who supplied a number of soil samples and explained their classification.

[2] Gravel and coarse sand are first removed by sieving, the finest sieve used for the paste being 100 meshes to the inch.

where R is the radius, and L, the length of the tube, A and B, (which are now stresses per unit area on the wall of the tube), are independent of the values of R and L, provided that R and L are reasonable in value. The physics of the flow-curve in general is complex, and as this matter has already been discussed in detail, the discussion need not be repeated here (2, 3, 10).

For some time it was believed that the measurement of the slope and extrapolated intercept of the fourth region straight line [which were called "mobility" and "yield-value" respectively (2)], constituted a measurement of the "plasticity" of a material, though no exact definition was attached to that term. However, the term "plasticity" is a very ancient one; not only had "πλαστικός" a very definite meaning to the Greeks, but it is found that the same meaning, only rather more defined, is associated with the term by prac-

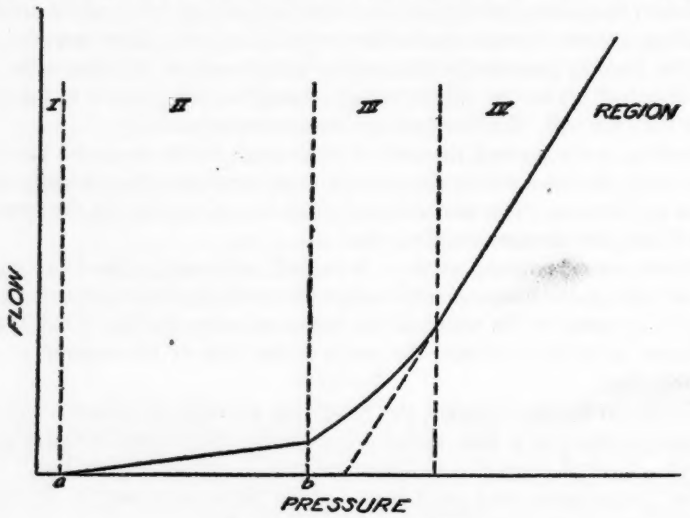

FIG. 1. FLOW CURVE OF SOIL

tical ceramists and others today. In a recent paper (4), this whole question has been discussed, and it was decided by the author that the following definition, given by Wilson (11), expressed, perhaps better than any other yet put forward, the idea underlying the term "plasticity," both with respect to its traditional and its modern requirements. Wilson definds plasticity as "that property which enables a material to be deformed continuously and permanently without rupture, during the application of a force which exceeds the yield-value of the material."

Now, it has been becoming increasingly clear for some time that plasticity defined in this way is *not* measured by mobility and yield-value; and yet it was felt that there should be some connection between plasticity and the flow-curve. In seeking for this connection, the following empirical fact was estab-

lished (4): *If pastes of clays in water are compared at such (different) concentrations of water that they show the same A-value, then the B-values measured at these concentrations are very closely related to the plasticity of the material, in the Wilson sense.* Since the test is still not fully understood, and since the use of the Wilson definition is, in a sense, arbitrary, it was decided to call this property "*flow-plasticity*," rather than simply "plasticity."

For convenience, the flow-plasticity is defined as the value of B in dynes per square millimetres, for a paste at such a water-content that it gives an A-value of 1 dyne/mm.^{2} In certain cases, however, 1 dyne/mm.^{2} is too high a value for A, for convenience and accuracy. For this reason, whereas B' will be written for the true flow-plasticity, B'_m will refer to a similar property, when A is m, instead of 1 dyne/mm.^{2}

In comparing two materials, the relative true flow-plasticities and the relative flow-plasticities at some value of A other than 1 should, of course, agree. This is not accurately the case: plasticity depends on the whole curve relating A to B for different concentrations, but the discrepancies are not great, and it is believed that, provided reasonable A-values[3] are chosen, the correlation with true plasticity is sufficiently close to be of considerable practical use.

The foregoing is a very brief description of the measuring and origin of flow-plasticity. For details, both in the theory and technique, the original papers (4, 5, 9, 10) should be referred to; but the discovery of a new method of measuring quickly, and with fair accuracy, something very closely allied to plasticity seemed of such significance with reference to soil work, that certain preliminary experiments were immediately undertaken. An outline of these experiments forms the subject of the present paper.

EFFECT OF LIME AND CHALK ON THE FLOW-PLASTICITY OF A HEAVY SOIL

It has already been shown (9) that if pastes of soils treated with chalk and lime are compared at the same moisture-content, the yield-values[4] are reduced, as compared with a control sample, to an extent depending on the time, and on the extent of the dressing. This reduction was shown to parallel a reduction in the force required to draw the plough through the soil. It is known that the addition of large dressings of chalk and lime make ploughing lighter; and since the less plastic the soil, the less the force required to deform the sod before its rupture by the mouldboard, and hence the less the energy wasted, it was thought that lime and chalk would be expected to reduce the flow-plasticity of a soil also. To test this prediction, a sample of Cornell University farm

[3] In actual practice, it is not necessary to adjust the A-value to exactly 1 dyne/mm.^{2} If a reading is taken at a value just greater than 1, and the material is then diluted and another reading is taken at a value rather less than 1, the B-value corresponding to $A = 1$ can be obtained from the other figures by means of a simple interpolation, since, over small ranges at least, A and B are linearly related.

[4] Intercept of the fourth region of the flow-curve extrapolated to the stress or pressure axis. Also called "rigidity" (or more correctly, "limit of rigidity") or "shearing strength."

soil (Dunkirk silty clay loam), taken from a plot which has been fallow for some years, and practically free of carbonates, was divided into a number of portions, and these were treated at the ordinary field condition of moisture with different amounts of chalk and lime.[5] Tests on flow-plasticity were made after 1–2 and 12–14 days respectively, and it was established that:

Lime, in quantities as small as 1 part to 1,000 reduces the plasticity of the soil.
This effect is more marked when the lime is finely ground than when it is coarsely ground.
Chalk reduces the plasticity, but to a lesser extent than does lime.
The reduction in plasticity is a slow process, being greater after a fortnight than after two days.

The results are given in table 1.

TABLE 1

*Results on tests of flow-plasticity**

TREATMENT	B' (1–2 DAYS)	B' (12–14 DAYS)
	$d/mm.^2$	d/mm^2
Control	10.6	10.6
1 part lime per 1,000	10.4	9.7
5 parts lime per 1,000	8.1	7.9
20 parts lime per 1,000	6.8	(8.8)†
20 parts lime per 1,000, but lime coarser ground	8.7	7.2
20 parts chalk per 1,000	8.0	7.8

* All flow-plasticity data given in this paper were obtained at a temperature of 25°C.
† This figure is unreliable, as there was a leak in the apparatus.

FLOW-PLASTICITY AS APPLIED TO THE STUDY OF THE SOIL-PROFILE

It is clear that, as the finer soil particles are leached through the soil, there will be changes in plasticity as we pass from one subhorizon of the soil to another. In general, for soils where the maturing process is a podzolization process, the *B* horizon will be expected to be more plastic than the *A*, as the finer particles of soil accumulate in the *B* horizon. Although this is indeed the case, it is very curious that in all four of the experiments which have been completed, "sticky-point" (7, 8) measurements have shown no increase in the amount of water the soil can hold in its most plastic condition in passing from the *A* to the *B* horizon. Although there is no direct relationship between the plasticity of a soil and its water absorption capacity, one would have expected that, since the finer soil particles do, in general, hold more water than the coarser ones, the sticky-points should have followed the plasticity figures. It

[5] It seems that the ceramists are already aware that "Carbonate of Lime reduces the plasticity of clay" (6, p. 27): but the matter does not appear to have been investigated in much detail.

is not known whether this phenomenon is at all common.[6] The results of measurements on soil profile samples are given in table 2.

TABLE 2

Measurements of sticky-points and flow-plasticity figures in virgin soils

HORIZON*	$B'_{0.5}$	M†
Penn silt loam (New Jersey)		
A_0	3.4	38.0
A_1	3.4	26.0
B_1	4.9	23.0
B_2	3.6	22.5
C	...	21.0
Dunkirk silty-clay-loam (New York)		
A	4.6	23.5
B	6.6	23.0
C	4.6(?)	20.0
Rough, stoney, and broken land (New York)		
A_0	4.9	....
A	6.5	....
B	7.3	....
C	3.7	....
Hagerstown silty-clay-loam (New Jersey)‡		
A	3.0	23.0
B_1	3.8	21.0
B_2	4.8	25.0
C	4.0	25.0
Volusia silt-loam (New York)		
A	3.2	34.0
B	3.7	31.5
C	2.7	23.0

* Since all gravel and even coarse sand has to be removed before the flow-plasticity test can be carried out, it is clear that measurements on the *C*-horizon are likely to be inaccurate. The interest lies chiefly in the *A*- and *B*-horizons.

† M = gm. of water per 100 gm. of mixture at concentration of maximum plasticity. Determined by heating in oven for 24 hours at 110°C.

‡ This soil was tested at rather too low an *A*-value. The results are not very accurate.

FLOW-PLASTICITY AS RELATED TO SOIL-TYPES

It is clear that a single measurement of the plasticity of a soil could not be related simply to a function depending on as many factors as does soil-type.

[6] Since sending this paper to press I find that this phenomenon has already been observed (see Baver, L. D., *Jour. Amer. Soc. Agron.*, 1930, 22: 935).

The plasticity would be expected to depend chiefly, if not entirely, on the texture of the soil, at any rate provided there was no great quantity of organic matter to confuse the issue. For this reason it was thought advisable to add to heavy soils, varying quantities of a standard fine sand as an inert material, thus measuring not only the flow-plasticity of the soil, but also that of each mixture, and determining the power of the soil to retain its plasticity on dilution with an inert material.[7] By plotting flow-plasticity against percentage of added sand, "dilution curves" characteristic of the soil can be obtained.

The sand is prepared in the following standard way:

Ground sand[8] contains no particle which will not pass the 100-mesh to the inch sieve, but it contains a good deal of silty material which may not be "inert" plastically. For this reason, 250 gm. of this sand was shaken in a tall cylinder, with distilled water made up to 1 liter. The mixture was allowed to stand for a quarter of an hour, and the unsettled material was then decanted, the sediment being filtered dry, then air dried, and bottled ready for use.

TABLE 3

*Soil dilution curves**

PER CENT ADDED SAND	B' FOR SOIL NUMBER				
	(1)	(2)	(3)	(4)	(5)
0	....	12.6	11.7	7.3	8.3
10	....	10.2	9.9	6.3	7.9
25	16.7	8.6	9.0	5.9	7.2
35	14.7	6.5†	7.9	5.7	6.9
50	10.5	4.9	5.8	4.6(?)	6.0
60	8.4	2.8(?)	4.9(?)	...	...
70	6.2	....	....	...	...

* Soils: 1. Whippany silty clay (N. J.). 2. Dunkirk silty clay loam (N. Y.). 3. Volusia silty clay loam (N. Y.). 4. Penn silt loam (N. J.). 5. Croton silt loam (N. J.). The soils were taken from the top few inches with no special sampling precautions, with the exception of the Penn silt loam, which was a *B*-horizon.

† This sample was 36 per cent sand.

Table 3 and figure 2 show characteristic figures and curves for a number of soils. It will be observed that these curves are remarkably linear, but, on extrapolation, do not meet at a single point. As 100 per cent sand is presumably without plasticity (or almost so), it is probable that the linearity is only apparent, and that if measurements could be made over wider ranges of sand concentration, the curves would be found to be curvilinear. It is clear that the capacity to retain plasticity on dilution does not follow hand in hand with plasticity itself. Thus two soils within the same textural group (e.g.

[7] This is not unlike the Bischof plasticity test (6, p. 47) which has been used for ceramic clays.

[8] Supplied by the Ottawa Silica Co., Ottawa, Ill.

nos. 2 and 3) may reverse the order of their plasticities on being diluted with sand, one being more plastic when both are "heavy," and the other more plastic when both are diluted. The soils chosen represent clearly marked textural types, as is plainly evident from their grouping in the figure. It is believed that these curves should be of interest in relation to soil classification.

It has been found (1) that soils which have been air dried do not always show regular "plug-flow," when made into a paste with water, and that the process of the recovery of regularity in this respect is a complex one. It is now believed by the writer that this loss of regularity is less common than was at first supposed. All of the soils used in experiments 2 and 3 were air dried, and in no case was the behavior so irregular as to prevent reliable measure-

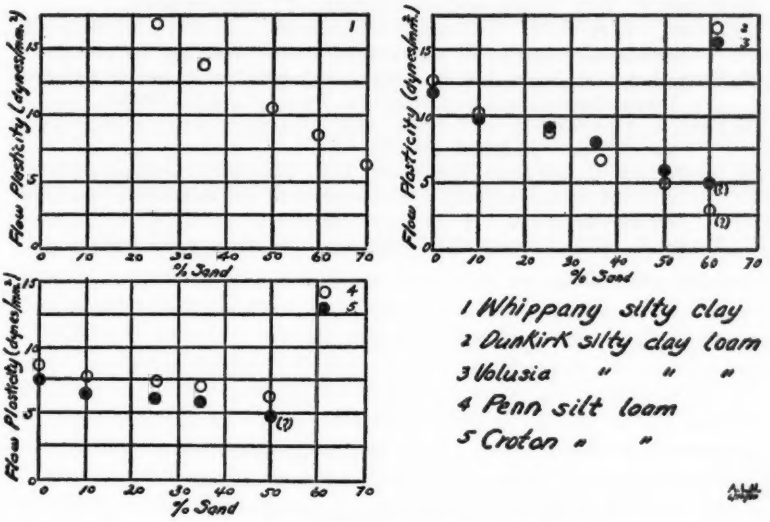

FIG. 2. CHARACTERISTIC SOIL DILUTION CURVES

ments being made, though several of the samples showed signs of irregularity. Thus the Penn silt loam pastes had to be sheared up to five or six times before a consistent, reproducible curve was obtained. At each pressure the system came to a dynamic equilibrium only after about a minute's flowing. In normal soils, this takes place within a few seconds.

SUMMARY

A brief desription is given of the way in which flow-plasticity is measured; and the relationship between flow-data in general, and plasticity in the sense defined by Wilson is discussed. It is claimed that flow-plasticity should give an interesting test for studying changes taking place in the physical properties of soils; and three cases, where changes are caused by (*a*) addition of chalk and

lime, (*b*) the normal leaching process, and (*c*) addition of sand to a heavy soil, have been investigated, and are quoted. It is shown that the plasticity of a soil is diminished by the addition of lime and chalk.

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THE STIMULATION OF LEMNA MAJOR BY ORGANIC MATTER UNDER STERILE AND NON-STERILE CONDITIONS

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The problem of the action of organic matter in soils and its direct influence on the green plant is by no means settled. Whether many of the essential elements are more available in organic combination, as indicated by Grandeau; whether the specific compounds released by decaying plant and animal life become available and act readily and directly on the plant as nutrients, stimulants, or poisons, as seems possible from the results of Schreiner and his coworkers at the Bureau of Soils (18, 19); whether the organic matter is the food of the microscopic life in the soil and this life forms compounds which can be assimilated by plants; or whether there are in the organic material certain "accessory substances" (4) of which minute quantities have great influence on growth, comparable with vitamins in animal life are questions to which the final answers have not yet been given.

Intimately bound up with the action of organic matter already in the soil is the function of organic fertilizers. The value of farmyard manure has been generally recognized to be greater than the value of the content of the chief elements in fertilizers. This has been ascribed to varying causes, including the increase in the bacterial activity in the soil to which manure is added. Bottomley (3) suspected the presence in the decomposing manure of accessory substances which would play an important part in the nutrition of plants. He experimented chiefly with Lemna and concluded that there existed "auximones" or growth-promoting substances, similar to vitamins and necessary for the growth of green plants.

In a previous communication (9) we reported experiments which showed that it is not necessary to add organic matter in order to obtain healthy reproduction of Lemna major (*Spirodela polyrhiza*) in solutions made from recrystallized inorganic salts and specially purified distilled water, and that the organic "auximones" postulated by Bottomley are not *essentials* for the growth of green plants. These results were later confirmed by other investigators, notably by Saeger (17), who used a diluted Knop's solution and Lemna major; by Wolfe (20), who used Shive's solutions and Lemna minor; and by Ashby in London (1) with the authors' medium and Lemna minor.

[1] Contribution from the department of chemistry. A preliminary note by the senior author on the sterilization of Lemna appeared in *Science*, 1930, 71: 268.

Although auximones were thus shown to be unlike vitamins for animals, in as much as they are not essentials for growth and reproduction, the stimulating action of very small quantities of organic substances was still unexplained. Livingston (11) pointed out the marked effect on the growth of plants of small amounts of organic matter when added to inorganic nutrient solutions; Mockeridge (14), Schreiner (19), and others have shown that decided stimulation occurred when extracts of soil or manure, or definite organic substances, were added to plant cultures. Ashby (2), who found stimulation of Lemna minor in our inorganic medium, considers the action of the organic matter to be catalytic in nature; Olsen (16) believes that it is connected with the existence of iron in organic combination in soil or manure extracts, or due to the greater availability of iron in such complex ions as those from ferric citrate. Wolfe (20) failed to get any increase in the reproduction of Lemna minor when he added a number of organic compounds to Shive's medium.

In order to investigate this stimulation of Lemna by organic substances it was necessary to obtain further information concerning the habits of the plant. The pH of the medium was determined in connection with the rate of reproduction, and an optimum of 4.8 found for the solution used (6). The plants were found to grow well under artificial light (5) without addition of organic matter. This was later confirmed by Ashby's work (1). Manganese has been claimed as an essential element for the growth of plants by McHargue and others (12). In this laboratory there was no indication that manganese was necessary for the Lemna; it was shown also that this element increased somewhat the weight of the plant and that there was an optimum concentration for this, but the manganese had no effect upon the rate of reproduction (8).

NON-STERILE EXPERIMENTS

With these details known it was possible to turn to the effect of organic matter. In the following experiments the solution contained, in millimoles per liter: 0.4 monocalcium phosphate, 8.0 potassium nitrate, 1.0 magnesium sulfate, 0.01 ferric chloride, and of manganese as manganous chloride 1 part in 10 million; the pH was kept at 4.8 by the addition of KOH where necessary. The plant cultures were grown in 250-cc. beakers in the sunlight. The beakers were placed in a thermostat which was kept at 25 C. The same technique was used for recrystallization of salts (7) and for the purification of distilled water as described previously (5). All glassware was pyrex.

The rate of reproduction is given as K in the formula

$$\log_{10} N/N_0 = K(t - t_0)$$

where N is the number of fronds at any time t (5). When log N is plotted as ordinate and t as abscissa the result is a straight line, the slope K indicating

the speed of reproduction. The "generation time"—the average time for the plant to reproduce itself—is given by the equation

$$\text{G. T.} = \frac{\log_{10} 2}{K} = \frac{0.3010}{K}$$

As the cultures were grown in sunlight, which varied from one experiment to the next, comparisons were made with controls in the inorganic medium made up as stated. The stock cultures have been growing for several years in this medium without the addition of organic matter.

Extracts were made of soil, of well-rotted farm-yard manure, and of alfalfa by maceration and twice digesting with distilled water at 70 C. for four hours with occasional shaking. The filtrates were combined and evaporated in

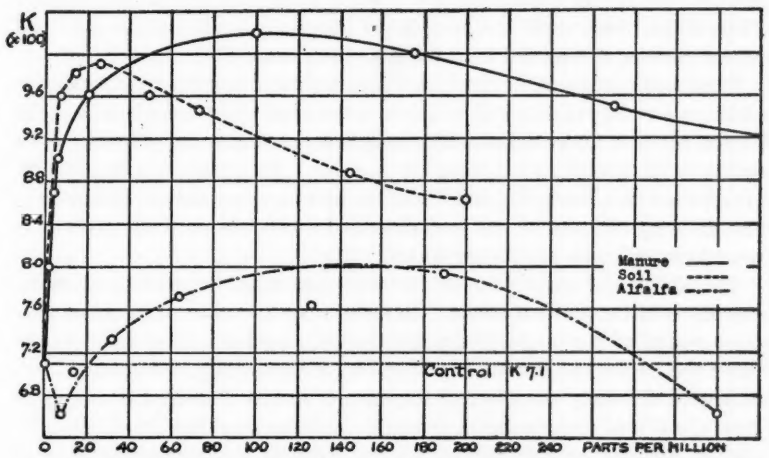

FIG. 1. RATE OF REPRODUCTION (K × 100) OF NON-STERILE LEMNA IN INORGANIC MEDIUM WITH EXTRACTS OF ORGANIC MATTER IN PARTS PER MILLION OF DRY MATTER

vacuuo at 65 C. They were then made up to a known volume and the concentration of solid matter was determined. The extracts were kept in the ice box in order to keep down the growth of microorganisms. Sufficient solution was added to the inorganic medium to give the desired amount of organic matter in 250 cc. and the pH was adjusted to 4.8. The plants were changed twice a week and the number of fronds counted.

Figure 1 shows the curves obtained when K is plotted on the number of parts per million of the three extracts. Both soil and manure extracts produced a rapid increase in the growth rate up to an optimum concentration, larger amounts lowering the speed of reproduction. Ashby (2), who used up to 20 p.p.m. of organic matter, did not find any decrease. The alfalfa curve indicates an increase in growth at some concentrations, but both large and small

amounts show a tendency to depress the rate of reproduction below the control. Signs of stimulation were observed also with extracts of yeast, carrots, and barley.

We obtained similar results in other inorganic media. Saeger (17) attempted to grow the Lemna in a solution made up of 1 gm. of each of KNO_3, KH_2PO_4, and $MgSO_4 \cdot 7H_2O$, 3 gm. of $Ca(NO_3)_2 \cdot 4H_2O$; 0.24 gm. of $FeCl_3$; in 6 liters of distilled water, but failed to get reproduction and health in the plants until the solution was diluted from 10 to 50 times. The pH of the undiluted solution, which is approximately 3.6, is much too acid for Lemna. We found that this medium had an optimum pH near 4.9 with a comparatively narrow range for good growth. When this undiluted solution was kept at the optimum pH and the manure and soil extracts were added, an increase in the rate of reproduction resulted, but it was smaller and the rise less abrupt than with our medium. The addition of asparagin and urea caused a depression of the rate at nearly all concentrations; this agreed with Wolfe's observations (20).

These results point to the conclusion that small quantities of organic extracts added to a variety of inorganic solutions can stimulate the reproduction of the Lemna not only under unfavorable conditions but also at the pH which is an optimum for growth in the inorganic solution. Bottomley (3), Mockeridge (14), Saeger (17), Ashby (2), and Olsen (16) have also reported this stimulation, and no inorganic solution has been described which will not be improved by some form and concentration of organic matter.

The addition of organic matter invariably increased the number of microorganisms in the nutrient media. In many cases the roots of the plants became coated with a fungus-like material which could not be washed off, and under the microscope showed large numbers of algae, fungi, and bacteria. To determine definitely the effect of the organic matter it seemed necessary to grow the Lemna under completely sterile conditions, so that the direct influence of different organic compounds and extracts could be studied free of bacterial action.

STERLIZATION

Hansteen (10) in 1899 attempted to sterilize Lemna minor by washing repeatedly with sterile water, and incubating in egg albumen. If there was no turbidity developed or ammonia evolved the plants were considered to be sterile. In repeating this we found that after washing the plants for one hour with sterile water, some of the albumen tubes remained clear. On transferring a small amount of the clear albumen to a nutrient agar, bacterial growth was invariably found after a few days.

Our next attempt was made by exposing the plants to ultra violet rays from a mercury vapor lamp. The technique was varied for time of exposure, distance from the light, wet and dry, in different concentrations of a large number of organic and inorganic chemicals, by alternate shaking and exposure with and without centrifuging, and by varying the temperature from the freezing point

upward. It was easy to kill the microörganisms, but with an exposure long enough to do this, the plants failed to reproduce in almost all cases. Further, there were indications that bacteria were frequently destroyed on the outside of the Lemna, but that some remained alive within the tissues. If a treated plant was dragged across the surface of an agar plate, growth often occurred only at the edges of the plant; also plates which showed no bacterial growth after several days produced colonies when the plants were macerated.

Two chemicals gave promise of complete sterilization when used with the ultra violet light. Potassium mercuric iodide K_2HgI_4 has been recommended as a germicide by Macfarlan (13) and others because the presence of organic matter does not reduce its germicidal action, and because it does not precipitate proteins. Bleaching powder was suggested as a possibility Wann.[2] Both of these chemicals, at one of the concentrations tried and with varying amounts of ultra violet light, gave a frond which remained alive and around which no bacterial growth developed on the nutrient agar. These two were therefore investigated further and it was found feasible to dispense with the ultra violet light altogether.

After treatment with the potassium mercuric iodide or the bleaching powder solution the plants were washed with sterile water and transferred to flasks containing our inorganic solution together with 1 gm. of bacto-nutrient agar per liter. In this medium at a pH of 4.8 both the non-sterile plants and bacteria developed readily. Without the ultra violet light, after 15 to 60 seconds contact with a solution of K_2HgI_4, at a concentration of 1 to 1,000 of the inorganic medium, some plants reproduced and were sterile. Under the same conditions, but for a saturated solution, the $CaOCl_2$ gave slightly better results.

The final sterilization technique was as follows: a non-sterile Lemna frond from the inorganic solution was washed with sterile water and transferred by a fork-shaped platinum wire for 30 seconds to a freshly prepared $CaOCl_2$ saturated solution. It was then washed again and placed in an Erlenmeyer flask, with the usual cotton stopper, containing the sterile medium already described. These flasks were kept at 25°C., away from direct sunlight, for five or six days, when the plants in those that appeared sterile were transferred to fresh medium. The fronds can be grown by transferring them to the pure inorganic medium directly after washing, but the bacto-nutrient agar readily shows those which are non-sterile.

From 400 plants 30 lived and were sterile. The outer part of the frond gradually withered, but the buds that were put out in the reproduction seemed to be unharmed and continued to reproduce. Transfers were made twice a week to the bacto-nutrient medium and a number of cultures inoculated into the purely sterile inorganic medium. Particular care was needed in the changing process in order to prevent contamination; the transfers were made in a small room sprayed beforehand with $HgCl_2$ solution. The plants have been

[2] Dr. F. B. Wann, in a private communication.

growing for nearly a year in the sterile inorganic medium, and they are checked periodically for contamination. No growth was found on the bacto-nutrient agar, dextrose agar, bacto-nutrient broth, and other media. Plate 1, figure 1, shows the growth on the different media after about 10 days for the non-sterile Lemna from the inorganic solution, compared to the plants from the sterile cultures. Plate 1, figure 2, shows the Lemna in the inorganic solution in the Erlenmeyer flasks.

TABLE 1

Effect of organic matter on the reproduction of sterile and non-sterile Lemna

TREATMENT NUMBER	TREATMENT OF INORGANIC MEDIUM	$K \times 100$	CONDITION AT END OF EXPERIMENT*
45	Autoclaved 20 pounds 15 minutes	5.3	s.
47	Autoclaved 20 pounds 15 minutes	5.1	s.
48	Autoclaved + 80 p.p.m. non-sterile manure extract	6.2	n.s.
49	Autoclaved + 80 p.p.m. non-sterile manure extract	6.3	n.s.
50	+ 80 p.p.m. manure extract. Autoclaved	5.3	n.s. (contaminated)
51	+ 80 p.p.m. manure extract. Autoclaved	5.4	s.
52	+ 80 p.p.m. manure extract. Autoclaved + 1 drop bacterial infusion	6.5	n.s.
53	+ 80 p.p.m. manure extract. Autoclaved + 1 drop bacterial infusion	6.6	n.s.
54	+ 80 p.p.m. manure extract. Autoclaved + 1 drop bacterial infusion	6.7	n.s.
55	Autoclaved + 1 drop bact. infusion	5.5	n.s.
56	Autoclaved + 1 drop bact. infusion	5.5	n.s.
61	+ 80 p.p.m. manure extract. Autoclaved + 1 cc. inorganic medium in which non-sterile plants had grown	6.7	n.s.
62	+ 80 p.p.m. manure extract. Autoclaved + non-sterile plants	6.9	n.s.

* s. = sterile; n.s. = non-sterile.

EXPERIMENTS WITH STERILE LEMNA

Extracts of organic matter were prepared as before but were autoclaved at 20 pounds pressure for 15 minutes. When the non-sterile plants were added to the sterilized nutrient medium containing the organic matter, an increased rate of reproduction occurred, showing that the treatment did not destroy the capacity to stimulate. Ashby (2) also has noted that autoclaving the organic extracts did not impair their stimulating properties.

Preliminary experiments with the sterile plants and organic matter showed a complete absence of stimulation over the plants in the autoclaved inorganic medium, and in several cases reproduction was slower where the organic matter

was present. When the sterile inorganic solutions containing the soil or manure extracts were inoculated with a drop of a suspension containing bacteria from the non-sterile plant, the rate of growth was increased. Indications were, therefore, that the sterile plants without organic matter grew as well or better than with the extracts in the solution, and that organic matter which increased the growth of the non-sterile plants, might depress the reproduction rate in the absence of microörganisms.

These conclusions were tested in two different experiments. In the first, a comparison was made between the inorganic medium alone, and this solution with sterile and reinoculated manure extracts. Table 1 shows the effect on

TABLE 2

Effect of organic matter and bacteria on the reproduction of Lemna

TREATMENT NUMBER	TREATMENT OF INORGANIC MEDIUM	$K \times 100$	CONDITION AT END OF EXPERIMENT*
10	Autoclaved	5.0	s.
11	Autoclaved	5.1	s.
12	Autoclaved + 1 drop bouillon infusion with non-sterile plant	4.7	n.s.
13	Autoclaved + 1 drop sterile bouillon	3.7	s.
14	+ manure extract 80 p.p.m. autoclaved	5.1	s.
15	+ manure extract 80 p.p.m. autoclaved	5.3	s.
18	+ manure extract 80 p.p.m. autoclaved + 1 drop bouillon infusion	7.3	n.s.
19	+ manure extract 80 p.p.m. autoclaved + 1 drop bouillon infusion	7.1	n.s.
16	+ alfalfa extract 130 p.p.m. autoclaved	4.4	s.
17	+ alfalfa extract 130 p.p.m. autoclaved	4.4	s.
20	+ alfalfa extract 130 p.p.m. + 1 drop bouillon infusion	6.1	n.s.
21	+ alfalfa extract 130 p.p.m. + 1 drop bouillon infusion	6.1	n.s.

* s. = sterile; n.s. = non-sterile.

the rate of growth of the Lemna. The initial pH was 4.8 and the solution was changed twice a week for five weeks. The bacterial infusion for numbers 52 to 56 was made from a 3-day inoculation of the non-sterile plants into bouillon. One drop was added to each flask when the solution was changed.

Urea, acetamide, and creatinine were also added and sterilized. The urea depressed the growth of the sterile Lemna markedly, but the acetamide and creatinine had little effect. With the addition of the bacterial infusion there was a decided depression in the reproduction rate for all three.

The figures for K show that there was an increase in the rate of reproduction when the non-sterile manure extract (nos. 48 and 49) was added to the sterilized inorganic solution (nos. 45 and 47). When this extract was autoclaved (nos.

50 and 51) there was no increase in growth unless it was reinoculated with the bacterial growth from the non-sterile plants themselves (no. 62) or from the non-sterile plants in bouillon (nos. 52, 53, and 54), or with some of the solution in which they had grown (no. 61). One drop of the bacterial infusion alone in the inorganic medium increased the rate but little (nos. 55 and 56) so that the accelerated reproduction comes from the presence of both the extract and the bacteria. The presence of the microörganisms was distinctly unfavorable with the pure organic compounds used.

The second experiment ran for four weeks. A fresh manure extract was used and the result checked the former lack of increase when the sterile extract was added to the autoclaved inorganic medium. In this group alfalfa extract was included and again inoculation was needed before stimulation occurred. Table 2 shows the treatment and the growth rate constant.

A number of pure cultures of bacteria were obtained from the bacteriological department and sub-cultured in bouillon, but no one alone was better than the plant organisms when added to the inorganic medium with 80 p.p.m. of manure extract. The following were the pure cultures used in order of increasing stimulation: *Bact. coli; Cl. sporogenes; Ps. fluorescens liquefaciens; Bact. aerogenes; Cl. Welchii; staphylococcus aureus; B. subtilis; Erythro b. prodigiosus.* The reproduction constant ($K \times 100$) varied from 5.0 to 6.7, with the sterile controls in the inorganic medium giving 5.0 and 5.1.

CONCLUSIONS

In no case have we found a stimulation of the reproduction of the Lemna in the inorganic medium, either from pure organic compounds or extracts of substances containing organic matter, when the plants are grown under sterile conditions; in some cases, especially with the organic substances like urea and creatinine, there has been a depression of the rate of growth in the sterile solutions compared with the controls in the inorganic medium. Reinoculation with microorganisms from the non-sterile plants or from the soil or manure has increased the rate of reproduction except in a few cases. Inoculation with pure cultures of bacteria has given in general an increase, although one or two did not stimulate the growth; in no case was the increase as great as inoculation with mixed cultures from the non-sterile plant.

The sterile plants have invariably reproduced slightly faster than non-sterile when no organic matter was present. Mockeridge (15) found evidences of stimulation when dead cultures of Azotobacter were added to the inorganic solution, but we have found no significant increase with either dead or living bacteria when added to the sterile inorganic medium. These facts would indicate a parasitic nature for the bacteria rather than a symbiotic relationship with the plant. If there is no organic matter present except plant tissue, this serves for the bacteria; if there is other organic matter in the medium, the bacteria attack this and in many cases produce—by decomposition or synthesis—substances which stimulate the plant. This, however, is theory and

is negatived by the fact that if sterile and non-sterile cultures in the inorganic medium are changed only once a week, the comparison soon becomes markedly in favor of the non-sterile group for general appearance. On the other hand when the sterile plants were grown on an autoclaved suspension of Carrington loam they quickly began to die, whereas reinoculation caused excellent growth and rapid reproduction.

SUMMARY

Lemna major has been grown for several years in a purely inorganic medium under non-sterile conditions.

The rate of reproduction is increased by the addition of small amounts of extracts from manure and other organic substances, but the inclusion of the organic matter increased the number of microörganisms.

Attempted methods of sterilization included ultra violet light and germicides. A technique was worked out by which K_2HgI_4 and $CaOCl_2$ sterilized the plants.

Under sterile conditions extracts of organic substances which before stimulated now had no effect or depressed the rate of reproduction. On reinoculating, stimulation occurred as before. The growth of the sterile plants was always rather faster than the non-sterile in the inorganic medium.

Pure cultures of bacteria varied in their effect in the solution containing organic matter—some increased the rate of reproduction and some did not.

None of the pure organic compounds which were tried gave any stimulation, either under sterile or non-sterile conditions.

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PLATE 1

GROWTH OF STERILE AND NON-STERILE LEMNA

FIG. 1. Sterile and non-sterile Lemna after 10 days on different nutrient media. The culture on the extreme right is non-sterile.

FIG. 2. Sterile Lemna in inorganic nutrient solution.

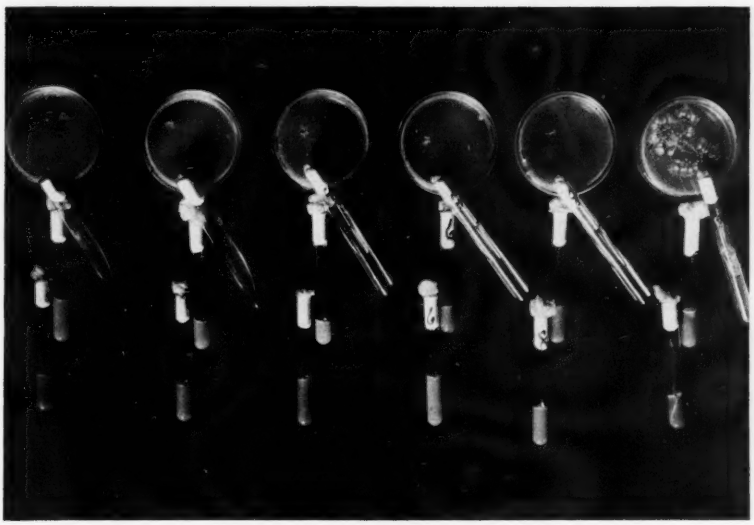

FIG. 1

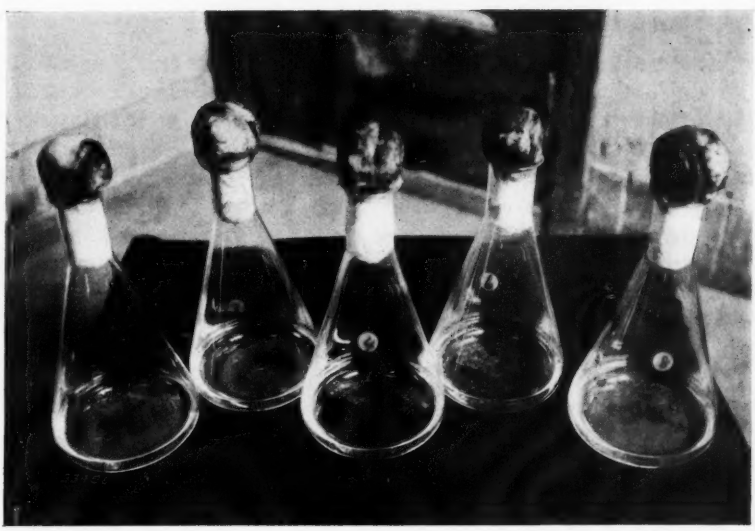

FIG. 2

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: V. ION ADSORPTION AND EXCHANGE[1]

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In the two preceding sections, parts III and IV of this series of papers, a number of isoelectric precipitates of aluminum and ferric "hydroxides," "silicates," "phosphates," and "humates" have been discussed in relation to the conditions governing their formation and to their composition. In the present and in subsequent sections we shall deal with the subject of ion adsorption and exchange by these materials. The isoelectric precipitates, prepared on a large scale for this work, are admirably suited, because they form natural series in which the various factors and functions vary in an ascending or descending order. Only by the use of such series will it be possible to carry out a systematic study of the phenomena of adsorption and to discover the underlying principles of such reactions.

THE CATION EXCHANGE CAPACITY OF VARIOUS COMPLEXES

We shall first study the capacity of the various precipitates for cation adsorption and exchange in neutral salt solutions. Later we shall study the adsorption of both anions and cations at various hydrogen-ion concentrations.

The isoelectrically precipitated "silicates" and "phosphates" were freed from the mother liquid by filtration but without washing. They were then dried at 65°C. and powdered. The "humates" were kept moist in the form of a stock suspension after most of the supernatant liquids were drawn off. One gram samples of the "silicates" and "phosphates" (air-dry basis) and one-half gram samples of the "humates" (105°C. oven-dry basis) were then leached on the filter each with 500 cc. neutral 0.5 *N* Ba-acetate solution then with 10 cc. *N* $BaCl_2$ and lastly washed free from Cl ions by hot water. The adsorbed Ba was then displaced with *N* NH_4Cl.

But it was found that although about 400 cc. NH_4Cl was sufficient to displace the Ba from the "silicates" and "humates," the Ba reaction persisted in the filtrate from the "phosphates" even after 1,200 cc. NH_4Cl solution had passed through. The following procedure was therefore adopted for the "phosphates:" Fresh samples were leached with 500 cc. neutral *N* NH_4-ace-

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

tate, then with 10 cc. NH_4Cl, and then washed with 90 per cent methyl alcohol [made neutral with a little ammonia as recommended by Kelly, Dore, and Brown (5)] until the disappearance of the Cl reaction. The adsorbed NH_4 ions were then displaced with $BaCl_2$ and the ammonia determined by distillation.

The results are given in tables 59, 60, and 61. The tables give the molecular ratios of acidoid (e.g. SiO_2, P_2O_5, and humus) to ampholytoid (e.g. sesquioxides) components as found in the various isoelectric systems. The

TABLE 59

Cation adsorption and exchange by isoelectrically precipitated aluminum and ferric "silicates"

SYSTEM NUMBER	COMPOSITION	ISOELECTRIC pH	LOSS ON IGNITION	SiO_2	EXCHANGEABLE Ba M.EQ./GM.	EXCHANGEABLE Ba M.EQ. PER M. MOL SiO_2
			per cent	*per cent*		
9	$Al_2O_3 \cdot (SiO_2)_{2.62}$	4.7	29.93	42.61	1.03	0.146
11	$Al_2O_3 \cdot (SiO_2)_{1.63}$	6.25	33.70	32.48	0.47	0.086
13	$Al_2O_3 \cdot (SiO_2)_{1.09}$	6.6	34.74	25.55	0.30	0.071
10	$Fe_2O_3 \cdot (SiO_2)_{2.26}$	4.95	23.60	35.22	0.98	0.168
12	$Fe_2O_3 \cdot (SiO_2)_{1.29}$	5.95	21.41	25.74	0.61	0.143
14	$Fe_2O_3 \cdot (SiO_2)_{0.79}$	6.35	20.65	18.24	0.44	0.146

TABLE 60

Cation adsorption and exchange by isoelectrically precipitated aluminum and ferric "phosphates"

SYSTEM NUMBER	COMPOSITION	ISOELECTRIC pH	LOSS ON IGNITION	P_2O_5	EXCHANGEABLE NH_4 M.EQ./GM.	EXCHANGEABLE NH_4 M.EQ. PER M. MOL PO_4
			per cent	*per cent*		
5	$Al_2O_3 \cdot (P_2O_5)_{0.857}$	4.9	29.15	38.50	1.844	0.340
7	$Al_2O_3 \cdot (P_2O_5)_{0.769}$	5.6	24.86	38.71	1.475	0.270
8	$Al_2O_3 \cdot (P_2O_5)_{0.482}$	6.45	28.40	28.68	0.875	0.216
8b	$Al_2O_3 \cdot (P_2O_5)_{0.242}$	6.65	32.00	17.10	0.300	0.125
6	$Fe_2O_3 \cdot (P_2O_5)_{0.914}$	4.0	25.20	33.50	2.370	0.503
6b	$Fe_2O_3 \cdot (P_2O_5)_{0.488}$	5.5	21.01	23.84	1.165	0.347
6c	$Fe_2O_3 \cdot (P_2O_5)_{0.244}$	6.05	19.91	14.25	0.722	0.359

"humates" however, are, expressed in terms of grams of humus to millimol sesquioxide.

Table 62 gives the exchange capacity of a series of natural soil colloids. The data are from a previous publication (9) in which the author established the relationship between the cation adsorption and the ratio of silica to sesquioxides.

The general agreement in the cation adsorbing power of the three classes of materials is highly interesting and should contribute much to an understanding of the mechanism of such reactions. The relationship of the silica/sesquioxide ratio to the cation adsorbing power, which the author has established for the

natural as well as for the synthetic "silicates" (11) applies in the same way to the "phosphates" and to the "humates." It will be noted that as the molecular ratios of P_2O_5 to R_2O_3 decrease and as the ratios of grams of humus to millimols R_2O_3 decrease the cation adsorbing and exchange capacity likewise decreases, exactly as in the silicates. This relationship appears to be quite general and might therefore be embodied in a generalized statement as follows: *The adsorption and exchange of cations, at pH 7.0, by soil colloids, in the same*

TABLE 61

Cation adsorption and exchange by isoelectrically precipitated aluminum and ferric "humates"

SYSTEM NUMBER	COMPOSITION: GRAM HUMUS M. MOL R_2O_3	ISOELECTRIC pH	PER CENT HUMUS (105° DRY BASIS)	EXCHANGEABLE Ba M.EQ./GM. b	EXCHANGEABLE Ba ON BASIS OF FREE HUMUS M.EQ./GM. a	EXCHANGE-MILLIEQUIV. HUMUS IN COMBINATION WITH Al OR Fe $a - b$	EXCHANGE-EQUIVALENTS HUMUS IN COMBINATION WITH 1 MOL R_2O_3	PER CENT FREE HUMUS $\frac{b \times 100}{a}$
52	$Al_2O_3 \cdot (Hum)_{1.305}$	4.5	91.6	1.827	2.62	0.79	1.13	70.0
53	$Al_2O_3 \cdot (Hum)_{0.553}$	5.15	81.7	1.055	2.33	1.27	0.83	45.4
54	$Al_2O_3 \cdot (Hum)_{0.265}$	5.5	68.9	0.600	1.97	1.37	0.53	30.5
56	$Al_2O_3 \cdot (Hum)_{0.140}$	6.2	53.9	0.411	1.54	1.13	0.29	26.7
58	$Al_2O_3 \cdot (Hum)_{0.070}$	6.8	36.8	0.332	1.05	0.72	0.14	31.6
55	$Fe_2O_3 \cdot (Hum)_{0.277}$	4.55	60.5	1.330	1.73	0.40	0.18	77.0
57	$Fe_2O_3 \cdot (Hum)_{0.141}$	5.4	43.8	0.848	1.25	0.40	0.13	67.8
59	$Fe_2O_3 \cdot (Hum)_{0.070}$	5.95	27.9	0.553	0.80	0.25	0.06	69.2
	Free humus	....	....	2.857	....	....	....	....

TABLE 62

Cation adsorption and exchange by natural soil colloids

COLLOID	COMPOSITION SiO_2/R_2O_3	SiO_2	EXCHANGEABLE Ba M.EQ./GM. (108° DRY BASIS)	EXCHANGEABLE Ba M.EQ. PER M. MOL SiO_2
		per cent		
Bentonite	3.81	48.80	1.102	0.136
Fallon	3.82	52.57	0.947	0.109
Sharkey	3.18	52.05	0.796	0.092
Marshall	2.82	45.93	0.671	0.088
Sassafras	1.89	41.14	0.331	0.049
Norfolk	1.63	39.25	0.207	0.032
Aragon	0.55	15.86	0.164	0.062

state of aggregation increase with the increasing ratio of the acidoid to the ampholytoid constituents of the colloid.

It would seem that this general relationship can best be accounted for on the assumption that the acidoid and ampholytoid constituents exist in partial combination with one another in the form of compounds which are at the same time both acidic and basic, and that the uncombined acidoid valences constitute the seat of cation adsorption and exchange whereas the free basoid mol fraction is responsible for the adsorption of anions. We shall proceed on this assumption.

Since basoid colloids, that is, materials which would react with only anions at any pH, are unknown, the term "ampholytoid" is applied to the basic constituents. The sesquioxides are, as we have seen, ampholytoids and become strong acidoids in alkaline solutions. Lateritic soil colloids which show a very low cations exchange capacity at pH 7.0 adsorb, for this reason, great quantities of bases from alkaline solutions (10). The preceding statement applies therefore to pH values below that of the isoelectric point of the sesquioxides.[2]

The cation adsorption per gram colloid is, however, not a linear function either of the acidoid/sesquioxide ratio, which we would also not expect, or of the percentage of acidoid in the complex. There are two conditions which would cause the adsorption to depart from a linear relationship to the percentage of acidoid. In the first place the state of aggregation in the different materials might not be such as to leave the same proportions of the acidoid valences free and active. In the second place, and this is more certain, the acidoid and the ampholytoid constituents do not themselves enter into combination with one another to the same relative extent in the various complexes. Thus the number of free acidoid valences which are not in combination with the (by ordinary salt reactions) non-exchangeable ampholytoid, are not proportional to the total acidoid present, but vary with the acidoid/ampholytoid ratios.

This becomes quite evident when we calculate the exchangeable milliequivalent cations per millimol SiO_3 and PO_4 as in the last columns in tables 59, 60, and 62, and the percentage free humus as in the last column in table 61. It will be noted that in the colloids having a high ratio and formed at a low pH, the exchange per millimol SiO_3 and PO_4 is the greatest. This means obviously that a larger molar fraction of the acidoid remains free to enter into exchange reactions in the case of the more highly silicated and phosphated complexes.

The same holds for the humus complex, in which the percentage of free humus increases with an increase in the composition ratio as the isoelectric pH is decreased. The quantity of humus that has entered into combination with each mol sesquioxide is also greater the lower the isoelectric pH, just as in the case of the mineral complexes. We do not know the molecular weight of the humus complex, which obviously is an aggregation of several molecules, nor do we know its true equivalent weight as an acidic entity but we know its exchange-equivalent in the free state, which is 2.857 milliequivalents per gram. Knowing the percentages of humus in the various complexes, we can calculate, from their exchange capacities, the exchange—equivalents of humus which have combined with, or been inactivated by, the aluminum and iron. The results are shown in table 61.

[2] The methods of Hissink for determining the total saturation capacity T and the derived value $\frac{S:100}{T}$ assume therefore absurd proportions when applied to lateritic soils.

The number of exchange-equivalents of humus in combination with each mol of sesquioxide, which vary between 1.13 and 0.06, are apparently smaller than the number of equivalents of SiO_3 and PO_4 so combined. But it is possible that that part of the hydrogen which dissociates too slightly to be displaced by the cations of the neutral salt solution has been displaced by aluminum and iron. It is therefore impossible, by this method, to tell anything about the exact extent to which the humus occupies the valences of these ions. This applies to the silicated and phosphated complexes as well. We can not merely subtract the exchange-equivalents from the total equivalents of SiO_3 and PO_4 and say that the remainder is in combination with Al and Fe. Both of these anions exist in combination with hydrogen so slightly dissociated as not to be displaced by the cations of the neutral salt solution. Then there is the possibility, which, in the case of the natural colloids, is a certainty, that some of the otherwise (in exchange reactions) active acidoid valences are locked up in the interior of the particles. Kelly, Dore, and Brown have shown that if the natural colloids be sufficiently ground, all of the mono- and divalent metal cations are exchangeable (5).

The "non-exchangeable" cations present in natural colloids and which make up a general average of about two-thirds to three-fourths of the total mono- and divalent bases present (1) are therefore non-exchangeable because of their position within the crystal lattice or molecular aggregates. The synthetic "silicates" which have not had time to crystallize show for this reason a higher exchange-capacity. Their exchange capacity is even higher in the moist condition than when dried at 65°C., which was done with the intention of increasing their stability.

Comparing the exchange capacities of the synthetic colloids, we note that the phosphated and humated complexes possess the highest capacities, especially where the composition ratios are high.

A very interesting and instructive observation is made by comparing the exchange capacities of the aluminum and ferric complexes. The ferric complexes show a much greater power to adsorb and exchange cations. Although the percentage of acidoid is lower in the ferric than in aluminum complexes of the same molecular ratios, because of the high molecular weight of Fe_2O_3, the exchange capacities per gram are uniformly higher in all ferric complexes. The differences are best seen by comparing the exchangeable cations per millimol SiO_3 and PO_4 and the percentages of free humus. Only the last three aluminum "humates" are to be compared with the three ferric "humates," which have the same composition.

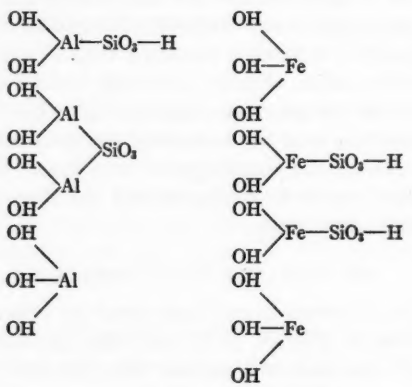
THE MECHANISM OF ION EXCHANGE

The cause of this difference in exchange capacities between the aluminum and ferric complexes is reflected in the exchange equivalents of humus in combination with one mol sesquioxide. For the last three aluminum "humates" the figures are 0.53, 0.29, and 0.14 as compared to 0.18, 0.13, and 0.06 for the ferric "humates." This means that the ferric compounds are

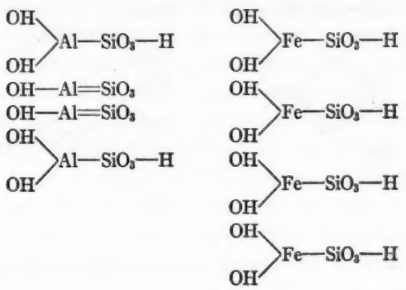
more hydrolyzed, that is, the OH ions displace more energetically the valences of other anions in the ferric than in the aluminum compounds. Now since these other anions are di- or polyvalent, one or more of their valences will be more easily displaced than the remainder. They are, therefore, not always bodily displaced from the complex but suffer only a partial displacement. *The free valences of these anions, partially linked up in stable combination constitute the seat of cation adsorption and exchange.*

The amphoteric colloids here studied represent salts of weak acids and bases containing residual H and OH ions. Their H and OH ion product must be less than the ion product of water ($K_w = 1 \times 10^{-14}$). *The strength of the acid and basic residue depends upon the dissociation constant of each. Where the one is high the other must be low.* $Fe(OH)_3$ *is a weaker base than* $Al(OH)_3$. *The former leaves therefore a stronger acid residue in the various amphoteric complexes. The ferric "phosphates," "silicates," and "humates" have therefore a higher cation exchange capacity because they contain more displaceable H ions and they have a lower isoelectric pH because they contain more active H ions than the corresponding aluminum complexes.*

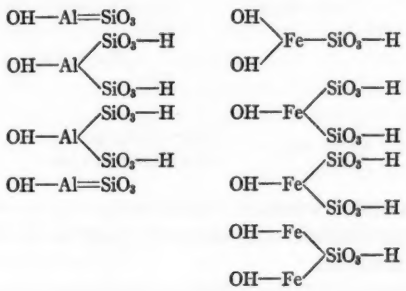
All this can hardly be represented by any formula, but it will be useful to indicate the structure of the various complexes in order to account for the differences in the exchange capacities according to the conception here developed. The amphoteric complexes will be represented in the acidoid-basoid form, that is, in the hydrogen-hydroxyl saturated condition. Either of these ions may, of course, be partially displaced by other cations and anions respectively. This happens to some extent even at the isoelectric point, as has been shown. At pH values above this point the progressive displacement of the H ion by metal cations increases rapidly. At pH values below the isoelectric point the OH ions are displaced by other anions. The following formulas, of course, represent nothing exact, but are merely meant to account for the general differences in the adsorbing power:



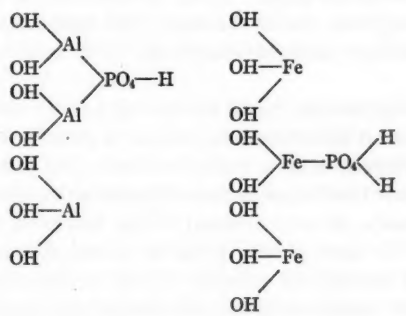
$\frac{SiO_2}{R_2O_3} = 1$ Cation adsorption low
Anion adsorption high



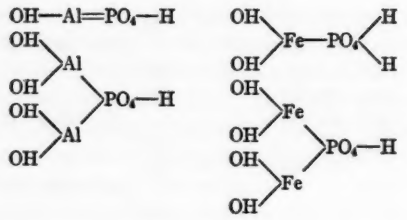
$\frac{SiO_2}{R_2O_3} = 2$ Cation and anion adsorption intermediate



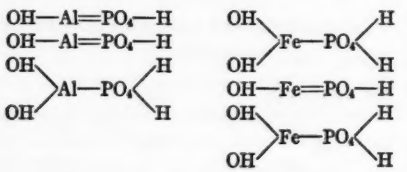
$\frac{SiO_2}{R_2O_3} = 3$ Cation adsorption high
Anion adsorption low



$\frac{P_2O_5}{R_2O_3} = \frac{1}{3}$ Cation adsorption low
Anion adsorption high



$\frac{P_2O_5}{R_2O_3} = \frac{2}{3}$ Cation and anion adsorption intermediate.



$\frac{P_2O_5}{R_2O_3} = 1$ Cation adsorption high
Anion adsorption low

These formulas represent molecular ratios which can be expressed in whole numbers. Any intermediate composition is possible if a sufficient number of molecules be considered.

The author has shown (10) that while the adsorption of the cations increases with the silica sesquioxide ratio in the natural colloids, the anion adsorption increases in the reverse order. The preceding formulas account for this behavior because the acidity and the basicity of the complexes, as here presented, vary in the inverse order. It will be seen that, in the assumed structure, the ferric complexes are at the same time more acidic and more basic than the corresponding aluminum complexes. This is all in accordance with their behavior.

Some soil investigators (6) would ascribe soil acidity and cation exchange to the existence of an alumino-silicic acid of a definite composition. The author cannot, on experimental as well as on theoretical grounds, share in this viewpoint. We have here before us three different series of colloidal aluminum and ferric compounds, all very different in the nature of their acid radicles and which show the same general behavior, chemically as well as electrokinetically, as the natural soil colloids. Yet it is doubtful whether anyone would ascribe these properties to the formation of any particular alumino-or ferric-silicic, phosphoric, or humic acids. *It seems quite obvious that we are dealing with colloidal complexes represented by a continuous gradation in composition as well as in properties.*

It is true that soil colloids differ from the synthetic products by being more

resistant to the action of acids and alkalies. But this does not prove, as has been maintained,[3] that the former are different compounds from the latter. Single substances often show very great differences in resistance to the action of solvents. Ageing, which brings about a change in the state of aggregation, may alone be responsible. Soil colloids are at least to some extent crystalline, as has lately been brought out by two interesting investigations by Hendricks and Fry (4) and by Kelly, Dore, and Brown (5). The crystalline materials appear to differ, as does the composition of the colloids, with the climatic conditions and the degree of weathering. The composition of the crystal is evidently affected by the composition of the complex from which it is formed. The analysis of "purified" materials has failed to show a stoichiometrically definite composition. This is not surprising, for although a constant ratio probably obtains within any one crystal, such will not be the case in the adsorption layer, which is very large in highly dispersed materials. On the surface of a silicate crystal a large number of the silicate ions will be displaced by phosphate, humate, hydroxyl, and a host of other anions.

A complete displacement (as distinguished from a fractional displacement) of silicate ions by OH ions and the subsequent loss of the former from the soil must lead to a decrease in the cation adsorption and exchange power, because the adsorption layer will then largely consist of free sesquioxides which do not combine with cations at a pH of 7.0. This condition is exemplified by the highly weathered tropical or subtropical soil colloids. These have a low silica/sesquioxide ratio and a low exchange capacity and are yellow or red as a result of free ferric oxide.

The sesquioxide layer on the surface of the particles formed by this displacement may be removed by peptisation with a hot, saturated $AlCl_3$ solution. An ash-gray silicate residue is then obtained in which the silica/sesquioxide ratio is higher and which possesses a higher cation adsorption and exchange capacity. Six soil colloids, all with a silica/sesquioxide ratio below 2.0 and of a rusty red color, except the Norfolk which is yellow, were thus treated. Following the treatment the $AlCl_3$ was removed by washing with 0.05 *N* HCl. The results are shown in table 63.

Whether the treatment lasted 3 days or 60 days made little difference. In all cases the composition of the ash-gray residues is not very far removed from a silica/sesquioxide ratio of 2.0, which is that of kaolinite and halloysite. X-ray analysis has also indicated, in highly weathered colloids, a structure similar to that of halloysite (4, 5).

The cation exchange capacity of the ash-gray residue was, in the case of the Norfolk colloid, 0.425 as compared to 0.207 milliequivalents per gram in the original material, an increase of 100 per cent. The power to adsorb anions such as the Cl and SO_4 ions from acid solution was, on the contrary, com-

[3] By Dr. E. Truog at the 1928 meeting of the American Society of Agronomy. Washington, D. C.

pletely destroyed by the treatment (10). From this it is quite obvious that the cation adsorption is caused by a combination with the acidic constituent while the anion adsorption is brought about by a combination with the basic or ampholytoid constituent.

A displacement of the silicate ion by the phosphate might be expected to increase the cation exchange capacity since the phosphated complex possesses this capacity to a higher degree. A displacement of a di- or polyvalent anion by a monovalent anion should theoretically reduce the cation exchange capacity, since a monovalent anion in combination with the ampholytoid would have no free primary valence available for the exchange. Residual valences may, however, be active. Experiments are in progress to test this.

A fractional displacement of the silicate ion without its complete detachment from the complex and removal from the colloid should increase the cation exchange capacity because this would result in a greater number of free acidoid valences. The "build-up" in the exchange capacity of orthoclase and of artificial and natural colloids in alkaline solutions as reported by

TABLE 63

The silica/sesquioxide ratio of soil colloids before and after treatment with a hot, saturated $AlCl_3$ solution

TREATMENT	SILICA/SESQUIOXIDE RATIOS OF SOIL COLLOIDS					
	Aragon	Cecil	Norfolk	Orange-burg	Chester	Sassafras
None	0.55	1.34	1.63	1.71	1.79	1.89
$AlCl_3$, 3 days	2.08	1.81	2.19	1.98	2.08	2.13
$AlCl_3$, 60 days	2.17	1.92	....	2.08	2.18	2.33

Breazeale and Magistad (2), Burgess (3), and Magistad (8) may be thus explained. The OH ions partially displace the silicate ions from their union with aluminum and iron, giving rise to a greater number of free acidoid valences. Treating the Sassafras colloid for one hour on the steam bath with *N* NaOH and then titrating back to neutrality with HCl, increased the exchange capacity of the colloid about 300 per cent. The sample so treated was much more soluble in 0.05 *N* HCl than was the untreated colloid, pointing to an unlocking of the silicate bonds according to the following scheme:

$$OH—Al{=}SiO_3 + NaOH$$

$$\begin{matrix} OH \\ \quad\diagdown \\ \quad\quad Al—SiO_3—Na \\ \quad\diagup \\ OH \end{matrix}$$

If the cation exchange capacity depends upon the number of free silicate or other acidoid valences, then the entirely free silica gel should possess a higher cation exchange capacity than that of any silicate, just as the free

humus possesses a higher exchange capacity than any of the humates. But silica gel, as ordinarily prepared, possesses a very moderate cation exchange capacity. For dried silica gel an exchange capacity of only 0.236 milliequivalent per gram was found.

It was believed that a structure fine enough to prevent the free movement of the common, hydrated cations into the interior of the gel may be responsible for this phenomenon. To study this possibility 1 gm. of silica was precipitated from Na_2SiO_3 by neutralization with HCl in the presence of 10 gms. of cane sugar in a small volume of water. After being dried on the steam bath the gel was washed and treated in the usual manner with Ba-acetate. It was thought that if the gel were dehydrated in the presence of the large sugar molecules a coarser structure should result. This was also indicated by the great volume of this gel as compared to the sample dried in the absence of sugar. The exchange capacity was also increased by the treatment but only to 0.610 milliequivalent per gram, or about 150 per cent. A very large part of the silica was therefore inactive. How much of this inactive part exists in the anhydride form and how large a fraction of its displaceable hydrogen remains undisplaced at a pH of 7.0 we do not know. But it is quite obvious that the closeness in structure of nondispersing materials like silica gel and the permutites affects the penetration of ions. Wiegner and Muller (14) found only a very slight adsorption of methylene blue by the permutites whereas in the case of the high-disperse soil colloids the adsorption of this dye is considerable and proportional to their cation exchange capacity, as has been shown by the author (9). A lump of silica gel becomes dyed only on its surface when placed in a solution of methylene blue.

We have seen that the removal of sesquioxides by petisation with an $AlCl_3$ solution results in an increase in the cation exchange capacity and also that this capacity is increased by treatment with alkalies, which increase is believed to be due to a liberation of an additional number of silicate valences through a displacement from their combination with aluminum and iron by the OH ions. We shall now see that the opposite process—the introduction of additional quantities of aluminum and iron into the exchange complex—results in a lowering of the cation exchange capacity. This would, of course, follow from the exchange capacities of the various complexes studied but we shall use a natural colloid in order to show that what is true for the one holds for the other group of materials.

In the previous section 1-gm. bentonite samples were isoelectrically flocculated with 4.0 millimols $AlCl_3$ and $FeCl_3$ respectively. This means that 0.2044 gm. Al_2O_3 and 0.320 gm. Fe_2O_3 entered each gram of bentonite. The isoelectric pH values were 6.75 and 6.5 respectively.

The cation exchange capacities in milliequivalents per gram bentonite were as follows:

Original bentonite	*Bentonite — Al_2O_3 complex*	*Bentonite — Fe_2O complex*
1.002	0.429	0.970

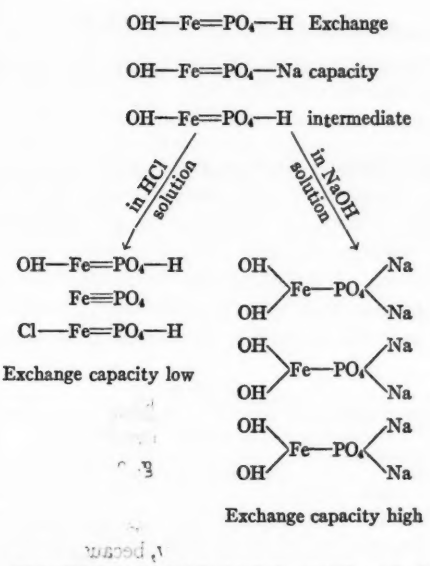
The aluminum ion has combined with and made inactive 57 per cent of the active silicate valences in the bentonite whereas the ferric ion has only inactivated about 3 per cent. The cation exchange capacity is therefore higher in the ferric complex than in the aluminum complex, just as we found it to be in the silicated, phosphated, and humated compounds of aluminum and iron. In the aforementioned complexes the bentonite plays the part of the acid anions of the previous experiments. It is also in reality a complex silicate ion. The exchangeable cations have been partly displaced by the Al and Fe ions which are not re-displaceable by the neutral salt treatment. The aluminum ions are more active in this respect than the ferric ions because the OH ions displace the silicate ions from their ferric combination more energetically, thus leaving a greater number of free silicate valences in the ferric complex.

By an alkaline solution it would be possible to displace a large part of the trivalent cations from their silicate combination and thus restore the exchange capacity of the bentonite. Upon acidifying, a recombination will, however, take place, the extent of which will depend upon the pH. A shifting in bonds must take place with each change in the H-ion concentration. The reaction between colloidal ionogens is, however, slow because of their non-diffusibility. Equilibrium proceeds slowly, therefore, in the wake of any change in the ionic environment. Thus the cation exchange capacity will be different depending upon whether we start the neutral salt treatment on acid or alkaline materials. On the acid side the number of bonds between acidoid and ampholytoid is greater than on the alkaline side. At the neutral point the number of such bonds is intermediate, but since equilibrium is slowly attained we get a higher exchange capacity at a pH of 7.0 when we approach this point from the alkaline than when we approach it from the acid side.

The influence of a change in the pH value upon the shifting of bonds may be illustrated in the case of a ferric "phosphate" complex having the composition shown at top of page 323.

A similar displacement takes place in the "silicates" and "humates." In the ferric "phosphate" complex this change can be observed by the change in color.

This conception of the colloidal complex explains a number of phenomena. It explains the great adsorbing power for bases from alkaline solutions and it explains the fact observed by the author (11) that the OH ion enters the complex together with the cation. From what has been said it is clear that the exchange capacity of an amphoteric colloidal complex does not represent a constant quantity even at the same pH. The exchange capacity depends upon the manner in which the valences are linked within the complex. Any treatment, physical or chemical, may bring about a shifting in the bonds The soil colloidal complex is a dynamic thing and is never the same under any two sets of conditions.



THE RELATION BETWEEN THE ISOELECTRIC POINT AND ION EXCHANGE

In the foregoing we have studied the cation exchange at a pH of 7.0. We have seen that the lower the isoelectric pH of the colloid, that is, the farther removed this pH is from pH 7.0, the greater the cation exchange capacity. Aluminum "hydroxide" (precipitated from the chloride) is isoelectric at or about pH 8.0. It is electropositive at pH 7.0 and showed no trace of cation exchange at this pH. How is the ion exchange related to the isoelectric point? What happens to the ion exchange, anion as well as cation, as we approach and pass this point from the negative to the positive side or vice versa? Since quantitative experiments dealing with these questions will be presented and discussed in the succeeding section we shall confine ourselves in the remaining space to a few qualitative experiments.

A number of aliminum "silicate" suspensions were prepared by mixing 100 cc. containing 1.0 millimol $AlCl_3$ with 100 cc. containing 1.5 millimol Na_2SiO_3. The pH was adjusted to cover a wide range by adding NaOH to the silicate or HCl to the chloride before the mixing of these solutions. The degree of flocculation was noted and cataphoresis measurements were made as shown in table 64. To 20-cc. portions of the various suspensions were then added 5 cc. water in one of the series and 5 cc. normal salt solutions in other series, and the pH determined colorimetrically in each as shown.

We note that all the salts give rise to an exchange acidity in the strongly negative suspensions whereas in the strongly-positive suspensions an exchange alkalinity is developed. The power of the various cations to displace hydrogen is, as far as the pH values are accurate, the following:

$$Li < Na < K = Mg < Ca < Ba$$

The power of the anions to displace the OH ions is, for the two ions used:

$$Cl < SO_4$$

How far the two kinds of displacements overlap can be learned only by a quantitative determination of all the ions in the solution at equilibrium. This work will be reported later. It will be noted that the strongly adsorbed SO_4 ions develop an exchange alkalinity at a pH at which the original suspension is still highly negative. It is obvious that the charge of the colloid was affected and even that the isoelectric point was displaced by the various salts. In the presence of so much electrolyte the cataphoresis cannot be determined

TABLE 64

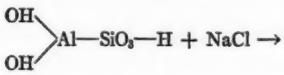
The exchange reaction at various pH values in a negatively and positively charged aluminum "silicate" and the lytropic effect of the ions

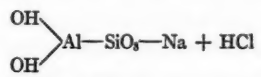
NUMBER	0.1 *N* NaOH	0.1 *N* HCl	FLOCCULATION	μ/SEC. 1 VOLT/CM.	pH AFTER 5 CC. WATER OR *N* SALT SOLUTION WAS ADDED TO 20 CC. OF THE VARIOUS SUSPENSIONS:							
					Water	LiCl	NaCl	KCl	$MgCl_2$	$CaCl_2$	$BaCl_2$	Na_2SO_4
	cc.	*cc.*										
1	2.0	....	0	.....	7.8	7.4	7.2	7.0	7.0	6.95	6.8	7.2
2	1.0	....	0	.....	7.4	...	6.9	...	...	....	6.55	6.95
3	...	1.0	0	.....	6.7	...	6.55	...	...	....	6.3	6.55
4	...	2.0	Slow	−2.52	6.45	...	6.3	...	...	....	6.15	6.35
5	...	3.0	Instant	−2.24	6.2	...	6.1	...	...	....	5.95	6.17
6	...	3.4	"	−1.21	5.7	...	5.6	...	...	....	5.45	6.0
7	...	3.6	"	+0.74	4.95	...	5.0	...	...	....	4.95	5.4
8	...	3.8	"	+1.38	4.75	...	4.95	...	...	....	4.85	5.3
9	...	4.0	"	+1.59	4.5	...	4.85	...	...	....	4.85	5.1
10	...	5.0	Slow	+1.92	4.3	...	4.6	...	...	....	4.62	4.95
11	...	6.0	0	+2.27	4.2	...	4.5	...	...	....	4.6	4.8
12	...	10.0	0	.....	3.9	...	4.3	...	...	....	4.38	4.6

without non-polarizing electrodes. But it is certain, from what has already been shown in the case of sulfated systems, that the SO_4 ion did not displace the isoelectric point to a higher pH but rather to a lower value. The cataphoretic isoelectric point is therefore no dividing line between exchange acidity and alkalinity. The point at which the exchange acidity changes to an exchange alkalinity, or vice versa, which we might call the point of exchange neutrality, will depend upon the relative displacing power of the two ions of the salt. The cataphoretic isoelectric point we have assumed to represent that point at which the anionic and cationic dissociations are equal. (The isoelectric point is possibly also determined by the orientation of the solvent molecules at the interface.) The position of either point is therefore determined by the dissociation constants of the amphoteric complex formed with

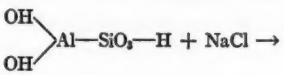
the two ions. But the effect is such that an ion which displaces the point of exchange neutrality in one direction must displace the point of electric neutrality in the opposite direction. Thus a slightly dissociating, and therefore strongly displacing, anion like the SO_4 ion, will carry the point of exchange neutrality to a higher pH but will displace the isoelectric point to a lower pH because of a suppressed anionic dissociation. A slightly dissociating, and therefore strongly displacing, cation will have the opposite effect.

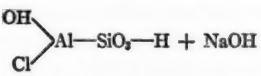
The exchange acidity formed at high pH values may be represented thus:





and the exchange alkalinity which is formed at low pH values thus:





We have now seen that an amphoteric colloid like aluminum "silicate" manifests an exchange acidity at higher pH values whereas at lower pH values the neutral salt reaction passes through a point of exchange neutrality and then develops into an exchange alkalinity, that is, cation exchange predominates at high pH values whereas anion exchange predominates at low pH values. An important question now is this: does this behavior, like so many of the others that we have studied, apply to the natural soil colloids as well as to the synthetic materials? Theoretically the amphoteric soil colloids, which possess a low silica/sesquioxide ratio and have an isoelectric point within the usual range of soil reaction, should show an exchange alkalinity at low pH values. There are a number of such colloids especially in the lateritic type of soils. One such soil, the Nipe clay from Oriente Cuba[4] has been studied in respect to this behavior. The electrodialyzed soil had a pH of 5.95 in water and a pH of 6.5 in *N* Na_2SO_4. When the same sample was treated with 0.1 milliequivalent HCl per gram soil the pH values were 3.6 in water and 5.1 in 0.5 *N* Na_2SO_4. The exchange alkalinity was therefore considerable especially in the more acid condition.

[4] Analyzed by Glenn Edgington and kindly supplied the author by W. O. Robinson, both of the Bureau of Chemistry and Soils. This soil contained 10.19 per cent SiO_2, 15.84 per cent Al_2O_3, and 62.51 per cent Fe_2O_3.

The significance of this behavior in connection with certain methods of determining soil acidity, "avidity" of the soil acids and lime requirements, will readily be recognized. An acid soil having a high sesquioxide content will either show an apparent exchange acidity which is smaller than the real or it will show a negative exchange acidity when in equilibrium with a salt solution, as a result of a displacement of OH ions by the anions of the salt. Upon prolonged leaching with a neutral or alkaline solution the adsorbed anions will, however, be largely or completely redisplaced by the firmly associating OH ions.

Soils in which the colloidal complex has a low silica/sesquioxide ratio and low cation exchange capacity have a higher pH when completely unsaturated with bases than do soils in which the aforementioned ratio and capacity are high. At a given pH, say about 5.0, the degree of base saturation is much lower in the former than in the latter type of soils. There is, therefore, no correlation between the pH and the degree of base saturation, as has recently been conclusively shown by Pierre and Scarseth (13). All this and many other phenomena discussed in the literature become comprehensible in the light of the behavior of the variously composed complexes. A complex having a low silica/sesquioxide ratio, and a low cation exchange capacity at a pH of 7.0 is not, at this point, far removed from its isoelectric point. At or slightly below the isoelectric point the cation exchange capacity must approach the vanishing point. This explains the low exchange capacity of such colloids at a pH of 7.0, it explains the rapid decrease in the degree of base saturation with a decrease in pH, and it explains the high pH at complete unsaturation, all as compared to colloids having a high silica-sesquioxide ratio and which have no isoelectric point, i.e., are not amphoteric, or have this point at a very much lower pH.

It will be recalled that the higher the acidoid/ampholytoid ratio the greater is the free acidoid mol fraction as measured by the number of milliequivalents exchangeable cations per millimol SiO_3 and PO_4. This evidently means more active acidoid hydrogen in the high ratio complexes because the least active hydrogen will be the last to be displaced by the ampholytoid valences. The unsaturated, highest ratio complexes react therefore most acid. In the foregoing the silicate ion has been represented as divalent, but it may be tetravalent like $H_4Si_3O_8$ or even higher associations. We may then account for all degrees of active hydrogen depending upon the (average) number of ions displaced by aluminum and iron.

THE DONNAN EQUILIBRIUM IN AN AMPHOTERIC COLLOID

In the electronegative condition the colloid particles are surrounded by a swarm or atmosphere of cations which have dissociated from the acidoid group of the colloid. These ions are hydrogen and metal cations, the relative proportion of each depending upon the degree of base saturation, i.e., upon the pH. In the electropositive condition the ion atmosphere consists of anions dis-

sociated from the basoid group of the colloid. If the colloid has been acidified with HCl then the Cl anions will predominate.

Now this difference in the composition of the micellar atmosphere will express itself in the unequal distribution of an ion, the H ion for example, within a suspension as compared to a clear filtrate or to an outside solution in equilibrium with the suspension. This distribution will be according to the Donnan equilibrium and will be such that the negative suspension, having H ions in the micellar atmosphere, will have a lower pH than the outside solution whereas the positive suspension, having Cl ions in the micellar atmosphere, will have a higher pH than the outside solution in equilibrium or, what is the same thing, the filtrate from the suspension.

The reasons for this difference have been explained in part I (12) of this series but will be here briefly recapitulated: In the micellar solution of the electronegative colloid there is a certain concentration, z, of H ions belonging to the micelle and which, for electrostatic reasons, are unable to diffuse into the external solution. Then there is a certain concentration, y, of free H ions belonging to the free acid, HCl in this case, and of course, an equal concentration, y, of free Cl ions. In the intermicellar solution we have only free H and Cl ions, the concentration of each being x.

Now the Donnan equation demands that the product of the concentration of any pair of diffusible ions must be the same in any part of the system at equilibrium. Hence

$$(x_{\mathrm{H}} \text{ outside})\ (x_{\mathrm{Cl}} \text{ outside}) =$$

$$(y_{\mathrm{Cl}} \text{ inside})\ (y_{\mathrm{H}} + z_{\mathrm{H}} \text{ inside})$$

or

$$x^2 = y\,(y + z)$$

Since

$$(y + z) > x$$

$$\mathrm{C_H} \text{ inside} > \mathrm{C_H} \text{ outside}$$

or

$$\mathrm{pH} \text{ inside} < \mathrm{pH} \text{ outside}$$

In the positive suspension where the micellar atmosphere consists of anions, e.g., Cl ions, there will be a concentration, z, of Cl ions belonging to the micelle, a concentration, y, of free Cl ions belonging to the free acid and an equal concentration, y, of free H ions. In the outside solution there will be a concentration, x, of free Cl ions and free H ions. Hence

$$(x_{\mathrm{H}} \text{ outside})\ (x_{\mathrm{Cl}} \text{ outside}) =$$

$$(y_{\mathrm{H}} \text{ inside})\ (y_{\mathrm{Cl}} + z_{\mathrm{Cl}} \text{ inside})$$

Since

$$x > y$$

$$C_H \text{ outside} > C_H \text{ inside}$$

or

$$\text{pH outside} < \text{pH inside}$$

In the latter case it is not necessary that the micellar anion be OH ions to account for the higher pH within the suspension. The excess of the acid anion in the micellar solution will force an excess of the free acid out into the external solution. Since the sesquioxides become negative at a pH where all but a small fraction of the acid anions, i.e., Cl, have been displaced by OH ions, it seems evident that the OH ions are, at most, slightly dissociated.

TABLE 65

The pH inside the suspension and in the solution outside a colloidium membrane at equilibrium, of aluminum "silicate" in the negative and positive condition

SUSPENSION NUMBER	M.EQ. IN 25 CC. SUSPENSION		FLOCCULATION	μ/SEC. 1 VOLT/CM.	pH OUTSIDE	pH INSIDE	pH OUTSIDE MINUS pH INSIDE	EXCHANGE REACTION	
	NaOH	HCl						In 0.5 *N* $BaCl_2$	In 0.5 *N* Na_2SO_4
1	0.08	.....	++++	−1.32	7.70	7.11	0.59	Acid	Acid
2	0.04	.....	++++	−0.76	7.13	6.82	0.31	Acid	Acid
3	0.02	.....	++++	±0.0	6.78	6.51	0.27	Acid	Acid
4	0.01	.....	++++	+0.84	6.56	6.31	0.25	Acid	Alk. (slight)
5	.....	.....	+++	+1.25	6.46	6.20	0.26	Acid	Alkaline
6	.....	0.01	+	+2.02	5.90	5.95	−0.05	Unaffected	Alkaline
7	.....	0.02	+	+2.42	4.90	5.70	−0.80	Alkaline	Alkaline
8	.....	0.04	+	+2.64	4.48	5.61	−1.13	Alkaline	Alkaline

To test this theory an aluminum silicate was prepared as in system 11 (see part III) by mixing 50 millimols $AlCl_3$ with 67.125 millimols Na_2SiO_3 but with only one-tenth the dilution. The supernatant liquid was drawn off and the floc was dialyzed for 30 days to remove the free electrolytes which otherwise would suppress the potential difference and the Donnan distribution. Then 25-cc. portions of the suspension containing 0.0675 gm. Al_2O_3 and 0.079 gm. SiO_2 $\left(\frac{SiO_2}{Al_2O_3} = 1.99\right)$ were adjusted to variouspHvalues by adding NaOH or HCl and were then placed in collodion bags made in large test tubes. These were placed in still larger test tubes, to which water was added (about 20 cc.) to the same level as inside the bags, and allowed to stand 2 weeks. The cataphoresis and the pH measurements were then made, the latter by the quinhydrone electrode. The results are given in table 65.

The negative suspension is more acid than the outside solution but for some reason, difficult to explain, this higher acidity of the suspension extends over on the cataphoretically, positive side. The cataphoretic isoelectric point is

at pH 6.51 and is, as it should be, well within the zone of flocculation. The isoelectric point with respect to the Donnan potential is at a pH about 6.0 since at a pH of 5.95 there is a slightly higher H-ion concentration in the outside solution than in the suspension. Below this pH the suspension is considerably less acid than the outside solution.

This discrepancy in the position of the two isoelectric points has also been observed by Loeb (7) in the proteins: The two points are apparently governed either by somewhat different factors or by the same factors but to a different degree. Why do the particles at a pH of 6.51 show no movement in the electric field and why do they move to the cathode at pH values of 6.31 and 6.20? In all three cases they possess a cation atmosphere. The particles should therefore be negatively charged and migrate to the anode as they do at higher pH values. If the particles are positive as their migration indicates, then how should we account for the cation atmosphere? Is there perhaps, a second outer atmosphere of Cl ions which for some reason, possibly because of a greater hydration, diffuse farther out into the dispersion medium? Then the cation atmosphere is merely a residual inner atmosphere, which nevertheless affects the quinhydrone electrode and also the indicators, because the pH values were checked with the indicator method.

Wiegner and Palmann (15), who have made an extensive and very interesting study of the effect of various colloids in respect to their acid or alkaline dispersion effect, would dispose of the aforementioned difficulty on the basis of their theory that the inner, as well as the outer, ionic layer consists of diffusible ions. The ions in either layer affect the electrode, so that if the colloid is positive, and has therefore an outer anion layer, its dispersion effect will nevertheless be acid as long as the H ions in the inner layer predominate over the OH ions in the outer layer. They do not consider the Donnan equilibrium. To account for the acid or alkaline dispersion effects, they assume the actual preponderance of H or OH ions in the two layers.

Although the author does not deny the adsorption of both of a pair of ions, originally extraneous to the colloid and the formation of a double layer of the ions thus adsorbed, he has here preferred to respresent the colloids as ionogens, dissociating into diffusible and non-diffusible ions since the evidences point overwhelmingly in that direction. This is done without ignoring the possibility of the existence of diffusible ions in the inner as well as in the outer layer. It is, however, difficult to understand why aluminum hydroxide should at a high pH adsorb Cl ions from HCl and be negative and at a low pH adsorb H ions from HCl and become thereby positive, when it can be shown that a combination with Cl ions actually renders the colloid positive.

The observation by Wiegner and Palmann (15, table 20) that the displacement of H ions by NaCl led to a weaker dispersion acidity may be explained on the basis of the suppressing effect of the high salt concentration according to the Donnan equilibrium. It can, of course, be shown that with nothing but Na ions in the micellar atmosphere, we shall, nevertheless, find a higher H-ion concentration inside than outside the micellar solution, because the high Na-ion

concentration within will force an excess of NaOH to the outside. But the Ca-permutite of Wiegner and Palmann, which was electronegative and of an alkaline reaction, produced an alkaline dispersion effect. We are therefore forced to conclude with them, that the micelles contain OH ions in the inner layer, fixed perhaps by "Gitterkräfte, Nebenvalenzattraktion, etc." but free to affect the hydrogen-ion determination. A further study in this direction will undoubtedly give us a better insight into the nature of the electrokinetic phenomena which are among the most difficult of interpretation.

SUMMARY

The cation exchange capacity of isoelectrically precipitated "silicates," "phosphates," and "humates" of aluminum and iron of varying composition ratios has been studied and compared with that of natural soil colloids of varying silica/sesquioxide ratios.

The exchange capacities, at pH 7.0, increase with the proportion of acidoid (SiO_2, P_2O_5, and humus) to ampholytoid (sesquioxides) in all the materials studied. The ferric complexes show a higher cation exchange capacity than the corresponding aluminum combinations.

The differences are explained on the assumption that the acidoid and ampholytoid constituents exist in partial combination with one another, resulting in compounds which are at the same time both acidic and basic. The free acidoid valences, uncombined with the ampholytoid valences constitute the seat of cation exchange.

The exchange capacity is not a constant quantity but can be altered by a shifting of the bonds.

The electronegative complexes give an exchange acidity with neutral salts whereas the electropositive complexes give an exchange alkalinity. The point of exchange neutrality does not, however, coincide with the isoelectric point but varies with the nature of the ions of the salt.

The Donnan equilibrium shows the micellar atmosphere to consist of cations in the electronegative condition and of anions in the electropositive condition but the cataphoretic and the Donnan isoelectric points do not appear at exactly the same pH.

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